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Heidelberg Coll., Tiffin, OH

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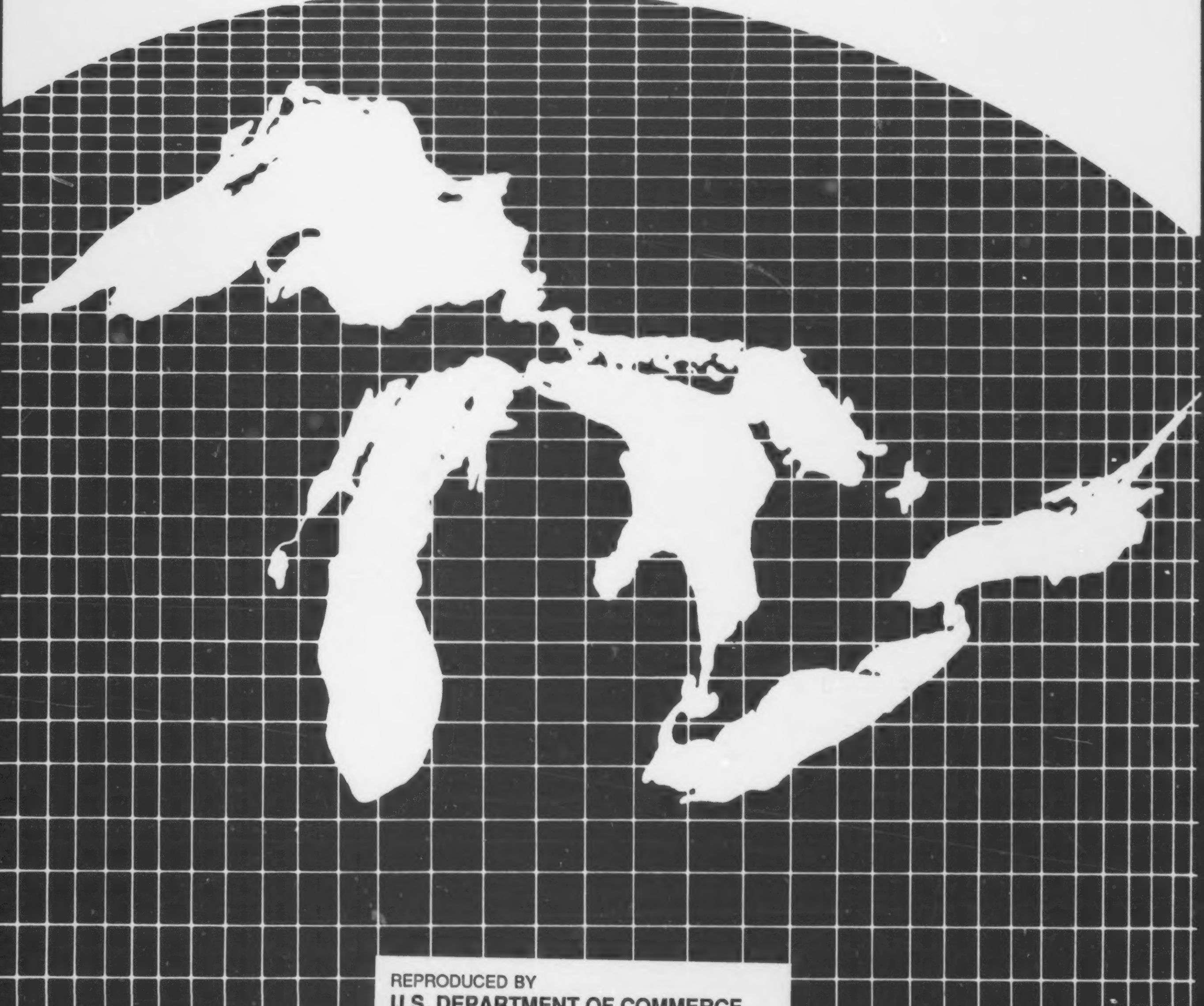

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SEDIMENT, NUTRIENT AND PESTICIDE TRANSPORT IN SELECTED LOWER GREAT LAKES TRIBUTARIES

by

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Grant numbers
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FOREWORD

The Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency was established in Region V, Chicago, to focus attention on the significant and complex natural resource represented by the Great Lakes.

GLNPO implements a multi-media environmental management program drawing on a wide range of expertise represented by universities, private firms, State, Federal and Canadian governmental agencies, and the International Joint Commission. The goal of the GLNPO program is to develop programs, practices and technology necessary for a better understanding of the Great Lakes Basin ecosystem and to eliminate or reduce to the maximum extent practicable the discharge of pollutants into the Great Lakes system. GLNPO also coordinates U.S. actions in fulfillment of the Great Lakes Water Quality Agreement of 1978 between Canada and the United States of America.

GLNPO has funded a major portion of the Lake Erie and Lake Ontario tributary studies whose results are summarized in this report. The intensive water quality data base gathered by Heidelberg College has contributed to our understanding of concentration and loading patterns in the Great Lakes Basin of pollutants associated with agricultural land use.

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16. ABSTRACT

Event sampling programs were conducted at 11 tributary monitoring stations in the Lake Erie and Lake Ontario watersheds during the 1982 - 1985 water years. Samples were analyzed for suspended sediments, nutrients and pesticides at 8 stations in the Lake Erie watershed and for suspended sediments and nutrients at 3 stations in the Lake Ontario watershed. The resulting data illustrate and quantify the effects of agricultural nonpoint pollution on regional surface waters. The data are analyzed with respect to both the concentration patterns of pollutants at the transport stations and the loadings of pollutants at the stations. Time weighted and flux weighted mean concentrations are presented, as are percentile distributions and concentration exceedency curves. Total loads, unit area loads and loading exceedency tables are also presented. Relative to tributaries in other agricultural regions, the concentrations of nitrates and pesticides in northwestern Ohio tributaries to Lake Erie are particularly high.

These data, in combination with similar studies dating back to the 1975 water year, are used to illustrate the annual and seasonal variability in agricultural runoff. Since the study watersheds range in size from 11.3 to 16,395 sq.km. the data also illustrate the effects of watershed size on concentration patterns and on seasonal loading characteristics.

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A major grant to the Heidelberg College Water Quality Laboratory from the State of Ohio has allowed laboratory staff to devote time to the preparation of this report, while continuing the operation of the basic monitoring program and launching several new directions in our research program.

Above all, my thanks are extended to my colleagues in the Heidelberg College Water Quality Laboratory, whose skills and dedication have made this research possible. The field collections and analytical work have been directed by our Laboratory Manager, Jack Kramer, with the able assistance of chief technician Ellen Ewing and technicians Barbara Merryfield and Francine Turose. Most of the computer programs used for data analyses and presentation were written by R. Peter Richards. Kenneth Krieger provided editorial assistance and directed the tillage survey components of the study. Staff assistant Nancy Creamer and secretary June Huss have done most of the preparation of tables and figures and the typing of this manuscript.

SECTION 1

INTRODUCTION

Much of the water pollution now affecting the Great Lakes Ecosystem, including both the lakes themselves and the tributaries which drain into them, is derived from nonpoint sources. Nonpoint source pollution is a consequence of the interaction of two major processes which occur on the earth's surface -- the hydrological cycle and land use activities. As water condenses and falls to earth, it picks up both natural and man-made chemicals from the atmosphere. Upon striking the earth's surface, it encounters additional natural and manmade chemical substances characteristic of that surface's land use activities, whether it be forestry, agriculture, industry, transportation, waste disposal, or urban and suburban living. As water either flows over the land surface into streams, rivers or lakes, or permeates through the soil toward groundwater, it dissolves and carries with it the soluble chemicals characteristic of that land use. Raindrops impacting the soil and water flowing over the land surface can also suspend particulate matter, along with chemicals associated with these particulates, and carry them into surface water. Where the resulting dissolved or particulate chemicals interfere with human uses of surface or groundwater, or otherwise meet definitions of pollution, the offending substances are categorized as being derived from nonpoint sources and as constituting nonpoint source pollution. Nonpoint sources of pollution can yield both "conventional" pollutants, such as sediment, oxygen consuming wastes, and forms of phosphorus and nitrogen, and toxic substances, such as industrial solvents, pesticides and some metals.

Among the major land use activities, probably none has had, and is having, a greater impact on the surface of the earth than the conversion of large areas of natural vegetation into areas for agricultural production. Often this conversion and the subsequent utilization of land for crop production has been accompanied by significant degradation of both soil and water resources -- resources which are of fundamental importance to regional economies and quality of life, both presently and in the future. Increased erosion often accompanying agricultural land use not only depletes soil resources (Crosson and Stout 1983), but also degrades water quality through increased turbidity and sedimentation (Clark et al. 1985, Waddell 1985). As fertilizer use has increased, the transport of nutrients from soils to surface waters has also increased, accelerating the eutrophication of surface waters (Schaller and Bailey 1983, OECD 1985, Overcash and Davidson 1980). Increasing use of agricultural pesticides has introduced additional toxic substances into surface waters. Soluble nutrients and pesticides are also impacting groundwater quality in some areas (Hallberg 1986, Holden 1986). There is increasing concern about global environmental impacts that may accompany increasing food and fiber production to meet the needs of the increasing human population (The Conservation Foundation 1986).

In the United States, the impacts of agricultural land use on water quality are increasingly being recognized as a major water quality problem affecting both surface and groundwater. Numerous recent symposia (e.g., see U.S. EPA 1985a) and special reports (e.g., see Journal of Soil and Water Conservation 1985) have addressed this topic. Agricultural runoff is the major source of nonpoint source pollution, and nonpoint sources of pollution are viewed as the major cause of pollution affecting most streams, rivers and lakes in the United States (Dysart 1985).

That an awareness of the magnitude of agricultural nonpoint source pollution has only recently dawned in the United States is a consequence of several factors:

1. Most of the attention in water pollution abatement programs has focused on point sources of pollution, which typically are much more visible, subject to easier quantification and suitable for focused control efforts.

2. Most ambient water quality monitoring programs for streams and rivers are designed to characterize the impact of point sources of pollution, and they greatly underestimate the magnitude of nonpoint sources of pollution.

3. Only after significant implementation of point source control programs did it become apparent that many water quality problems remained, and that these could only be accounted for by nonpoint sources of pollutants.

4. The magnitude of agricultural pollution problems has probably increased since the 1960's with the extensive industrialization of U.S. agriculture, including its increasing reliance on fertilizers, pesticides, and intensive row crop production.

5. Quantification of the impacts of agricultural nonpoint source pollutants on regional water quality require detailed and long term sampling programs that focus on runoff periods. Such studies are very rare because they frequently are accompanied by high costs.

In the Lake Erie Basin, detailed, quantitative studies of agricultural nonpoint source pollution have been underway since the early 1970's. These studies came about as a consequence of the application of mass balance approaches to the development of water quality management programs for the lakes. Such studies require accurate tributary loading data for each lake. It soon became apparent that, for Lake Erie, intensive tributary sampling programs during runoff events were essential to the development of accurate loading estimates.

The major portion of monitoring programs aimed at quantifying agricultural impacts on regional water quality in the Lake Erie Basin have been conducted by the Water Quality Laboratory at Heidelberg College. Supported initially by the U.S. Army Corps of Engineers, the U.S. EPA's Environmental Research Laboratory in Athens, Georgia, and manufacturers of soaps and detergents, the laboratory developed sampling, analytical, and computational techniques which, since 1974, have been applied in a consistent fashion to the tributaries of Lake Erie (Baker 1984). In 1981, the U.S. EPA's Great Lakes National Program Office began funding the intensive tributary sampling studies, and expanded them to include three major tributaries to Lake Ontario, where accurate sediment and nutrient loading estimates were also desired. Also in 1981, pesticide analyses were added to the analytical program and additional support was received from pesticide manufacturers.

The study watersheds range in size from 11.3 to 16,395 sq km. As such, they are much larger than the plot and field sized landscape units which are typically used for much of the agricultural research aimed at evaluating both the agronomic and environmental suitability of various cropping management practices. The wide range in watershed size allows characterization of the effects of watershed size on patterns of pollutant loadings and concentrations. Studies of these larger landscape units have the advantage of providing direct evidence of the cumulative impacts of agricultural practices on regional water quality, as reflected in the streams and rivers draining the study watersheds. The disadvantage of large watershed studies is that it is difficult to attribute the observed pollutants to particular source areas within the watersheds. While the plot and field sized studies do facilitate assessment of the site specific agronomic and environmental effectiveness of particular management practices, it is difficult to predict regional water quality conditions by extrapolating from plot and field runoff studies. Both types of studies are needed and should, in fact, be integrated more closely.

This report describes the results of the tributary loading programs for Lake Erie and Lake Ontario for the 1982-1985 water years. It also provides some comparisons with the tributary loading studies in the Lake Erie Basin for the 1975-1981 water years that have been described previously (Baker 1984). The report illustrates many of the characteristics of agricultural nonpoint pollution from intensive corn and soybean crop productions.

SECTION 2

SUMMARY

Within this summary, quantitative values will be presented for the Maumee and Sandusky rivers since they deliver the largest loads of agricultural runoff to the Great Lakes. Data for the other tributaries will be described relative to the Maumee and Sandusky.

2.1 EFFECTS OF AGRICULTURAL RUNOFF ON AMBIENT STREAM WATER QUALITY

Much of the emphasis in agricultural pollution studies is on the loading of agricultural pollutants to downstream receiving waters. Loading studies require data on both pollutant concentrations and stream flow. However, while the pollutants are in transit, their concentrations within the streams and rivers can significantly impact ambient stream water quality. In this region, the concentrations of sediment, phosphorus, nitrate and pesticides that are present during storm runoff events constitute significant water quality problems. In addition, sediment deposition to the stream bed during storm events alters the stream habitat for extended periods following the event.

2.1.1. Sediment Concentrations

For the Maumee and Sandusky rivers during the 1982-1985 water years, the time weighted mean suspended sediment concentrations were 87 and 72 mg/L respectively, while the flow weighted mean concentrations were 197 and 182 mg/L. Time weighted means generally decreased as watershed size decreased but flow weighted means were independent of watershed size. Peak sediment concentrations increased as watershed size decreased.

High sediment concentrations degrade water quality in a variety of ways. Certainly the turbidity associated with high sediment concentrations constitutes an aesthetic pollutant. It also diminishes fishing success. By reducing light penetration, suspended sediments can depauperate communities of rooted aquatic plants. This, in turn, greatly alters the habitat for other members of aquatic communities, including fish. As sediments settle to stream or lake beds, they also alter that habitat, affecting both benthic and fish communities. Often the sediments settle in areas where they subsequently must be dredged, at high cost, to maintain navigation channels or to increase channel capacity and minimize flooding. High sediment concentrations increase the costs of water treatment at both municipal and industrial water intake plants. While sediments are not themselves "toxic" they can serve as either a source or a sink for toxic substances or nutrients, depending on the origin of the sediments. It has been estimated that the offsite damages from erosion on cropland in the United States amounts to $2.2 billion annually (Clark et al. 1985). The potential benefits of agricultural erosion control measures, that reduce the offsite damages of sediments, should not be ignored.

2.1.2. Phosphorus concentrations

The time weighted average total phosphorus concentrations for the Maumee and Sandusky rivers during the 1982-1985 period were 0.257 and 0.196 mg/L (as P) respectively. The flux weighted mean concentrations for the same time period were 0.432 and 0.388 mg/L . The time weighted mean concentrations were generally lower in smaller streams but the flux weighted means were similar.

Phosphorus is one of the plant nutrients that is primarily transported in association with sediment particles. Consequently, its concentration also increases during runoff events. It affects water quality when present in concentrations or amounts that stimulate an overabundance of growth by algae or higher aquatic plants. In river systems during runoff events, it is likely that light penetration, rather than phosphorus, is the major limiting factor to plant growth. Phosphorus from agricultural sources, in both its soluble and particulate forms, begins to directly affect water quality as turbidity decreases and plant growth begins. Sediment can serve as either a source or a sink for phosphorus, depending on the source of the sediments, the ambient phosphorus concentrations in the water column, and the chemical and biological environment of the sediments. Since most of the adverse water quality effects of phosphorus are in downstream receiving waters, there is more concern about nonpoint source phosphorus loading from rivers into lakes than there is about ambient effects in stream systems.

2.1.3. Nitrate-nitrogen concentrations

The time weighted nitrate-nitrogen concentrations in the Maumee and Sandusky rivers were 3.93 and 3.48 mg/L respectively. The flux weighted concentrations were 5.29 and 4.22 mg/L. These are unusually high mean nitrate concentrations and reflect the extensive use of tile drainage systems in this region. The smaller streams had similar flux weighted concentrations. The flux weighted mean for the Cuyahoga River, which drains urban and forested watersheds, was only 1.85 mg/L.

Nitrate-nitrogen concentrations increase during runoff events from cropland. Although nitrate-nitrogen is a major plant nutrient, it is generally less likely than phosphorus to be limiting to plant growth in most aquatic systems. As is the case for phosphorus, there is generally high turbidity present in rivers when nitrate concentrations are highest. In contrast with phosphorus, nitrate is very soluble and is not attached to sediment. In Lake Erie tributaries, the major ambient water quality effect of nitrate is on public drinking water supplies. Because of its solubility, it cannot be economically removed from drinking water. In the Sandusky River, nitrate-nitrogen concentrations have exceeded the safe drinking water standard for 12 consecutive years during the spring period. Overall, nitrate concentrations exceed the standard about 4% of the time in the Sandusky River. Other Ohio rivers serving as sources for public water supplies, such as the Maumee and Scioto, are similarly affected by high springtime nitrate concentrations.

2.1.4. Pesticide concentrations

During spring and early summer, many currently used pesticides are present in Lake Erie tributaries. As with many nonpoint pollutants, pesticide concentrations are highest during runoff events. In general, the concentrations of herbicides are much higher than the concentrations of insecticides, and concentrations of both are generally proportional to their usage. During the period from April 15 to August 15, 1985, the time weighted atrazine concentrations in the Maumee and Sandusky rivers were 2.7 and 6.4 µg/L respectively. The alachlor concentrations were 0.7 and 2.9 µg/L and the metolachlor concentrations were 2.0 and 7.2 µg/L in these same rivers. Cyanazine, metribuzin and linuron are also frequently present but at lower concentrations. In smaller tributaries peak concentrations of individual compounds often exceed 100 µg/L.

The herbicide concentrations in Lake Erie tributaries appear to be higher than in many other rivers draining cropland. The effects of these herbicides on ambient water quality remain uncertain. Because of the low acute toxicity, the relatively low persistence and the insignificant bioaccumulation of most herbicides, direct toxic effects on animal life in streams and rivers appear unlikely. However, the concentrations of herbicides observed in these streams are within the range where effects on both algal and higher aquatic plant communities could be expected. Such effects may already be manifest in the existing algal and rooted aquatic plant communities of this region's streams and rivers, and within their associated wetlands and bays. Changes in these plant communities could affect the fish and invertebrate communities in streams and rivers. Also the herbicide concentrations could possibly induce behavioral responses in animals that could be detrimental to these communities.

Most of the pesticides present in streams occur primarily in the dissolved state rather than attached to sediments. Consequently, the removal of sediments at drinking water treatment plants does not remove most pesticides. Since other aspects of conventional water treatment, such as chlorination, also do not remove or alter these compounds, finished tap water has very similar concentrations of these pesticides as does the raw water. At present, the U.S. Environmental Protection Agency has not established maximum contaminant levels in drinking water for any of the herbicides monitored in these studies, even though this set of herbicides makes up about 85% by weight of the herbicides used in Ohio.

Drinking water standards for several of the major herbicides are scheduled to be set by the federal government in the near future. For the present, several states are establishing their own drinking water standards and the National Agricultural Chemicals Association has also suggested interim health guidance levels for some compounds (NACA 1985). The concentrations of herbicides in Lake Erie tributaries do exceed some of these guidelines, for relatively short periods of maximum concentrations. Activated carbon can be used to remove these compounds at water treatment plants and research is underway to evaluate other possible treatment techniques. While the concentrations of nitrate and pesticides are particularly high in Lake Erie tributaries, groundwater contamination by these same chemicals in this region appears to be much less extensive than in other regions of the country, such as portions of Iowa, Minnesota and Nebraska.

2.2. POLLUTANT LOADING FROM AGRICULTURAL NONPOINT SOURCES

While the effects of agricultural runoff on ambient water quality of streams and rivers can be assessed in terms of pollutant concentrations, assessment of impacts on downstream receiving waters or of losses from agricultural lands requires measurements of pollutant loadings. This is accomplished by combining concentration data with flow data. Most of the export from agricultural watersheds and the associated loading to receiving waters occurs during runoff events when both stream flow and concentrations of agricultural pollutants are high. Accurate loading data are necessary for mass balance pollutant management programs.

2.2.1. Sediment loading

The mean annual sediment loads from the Maumee and Sandusky rivers are 1,120,000 and 269,000 metric tons, respectively, as measured at the transport stations closest to the lake. This amounts to 0.68 and 0.83 metric tons per hectare per year (0.30 and 0.37 short tons per acre per year) respectively. The sediment yields reflect about 10% of the gross erosion which occurs within these watersheds each year. Most of the erosion which occurs simply moves soils down slope within fields. However, some sediments are deposited in drainage ways, in stream and river channels, and on floodplains. The Agricultural Research Service has estimated that the off-site damages from erosion in the lakes states is about $2.87 per year per (short) ton of gross erosion. Based on the estimates of gross erosion in the U.S. portions of the watersheds emptying into the western and central basins of Lake Erie, the annual off-site damages from cropland erosion would be $67 million. Most of this erosion and these damages occur in Ohio.

2.2.2. Phosphorus loading

The mean annual export of total phosphorus from the Maumee and Sandusky rivers for the period of record is 2460 and 503 metric tons per year. Much of the water quality management effort in the Lake Erie Basin has been aimed at reducing phosphorus loading and the associated problems of eutrophication. The phosphorus loads measured at the river transport stations are used in the estimation of total phosphorus loading into Lake Erie. The river loads include the combined output of point and nonpoint phosphorus sources within their watersheds. Point source phosphorus inputs can account for no more than 16% and 11%, respectively, of the total phosphorus loads exported from the Maumee and Sandusky rivers. Following separation of the point and nonpoint sources for each river, the resulting nonpoint source unit area phosphorus loads are used to estimate nonpoint source loading from adjacent unmonitored watersheds. Using this procedure, it has been estimated that rural nonpoint sources contribute about 60% of the total phosphorus loads currently entering Lake Erie. The phosphorus reduction strategies adopted by the various states to meet Lake Erie phosphorus reduction goals are focusing on reducing rural nonpoint loading.

At approximately 1.5 kg/ha/yr, the unit area phosphorus export rates for the Maumee and Sandusky rivers are high in relation to national averages. Even so, the phosphorus export is equivalent to only about 10% of the annual phosphorus fertilizer application within these watersheds. The high export rates of soluble reactive phosphorus, particularly, during winter months, may represent a very significant portion of the bioavailable phosphorus loading to Lake Erie. Impacts of adoption of conservation tillage on both total and soluble phosphorus export need to be monitored very carefully, because some plot studies have shown increased phosphorus concentrations with conservation tillage.

2.2.3. Nitrogen loading

The mean annual nitrate-nitrogen export from the Maumee and Sandusky rivers amounts to 25,500 and 5,110 metric tons per year. Total nitrogen export, including both nitrate, ammonium and organic nitrogen averaged 19 and 20 kg/ha/yr respectively. These losses are also much higher than national averages, due primarily to very high exports of nitrate-nitrogen. The extensive use of tile drainage systems in these watersheds apparently accounts for the high nitrate export rates, as well as the high nitrate concentrations in area rivers. Total annual nitrogen export in surface water is equivalent to about 50% of the amount of nitrogen applied in fertilizers each year. While other sources of nitrogen exist in these watersheds, such as nitrogen fixation and rainfall, the nitrogen export through surface runoff nevertheless does constitute a significant loss to farmers. While the concentration of nitrate is increasing in Lake Erie, it is not currently viewed as a problem for public water supplies utilizing the Lake or for the biological communities of the Lake.

2.2.4. Pesticide loading

In 1984 the observed export, in metric tons, of atrazine, alachlor, metolachlor, cyanazine, and metribuzin from the Maumee River was 5.53, 4.99, 3.49, 2.90, and 3.32 respectively. In 1985, the export of these same herbicides from the Sandusky River was 1.21, 0.77, 1.52, 0.14, and 0.36 respectively. There is considerable annual variability in pesticide export, with the data cited above representing the largest annual loads from the 1983 to 1985 period.

The loadings of most current generation pesticides into Lake Erie, while large in comparison with other toxic substances, are not viewed as posing priority problems since they are less persistent and have less of a tendency to bioaccumulate than the priority toxic compounds. The major problems that may be associated with the loadings of these compounds relate to resulting concentrations in bays and wetlands. Although these compounds are not persistent, their continuing large volume use makes them consistent seasonal components of the chemical environment of streams, bays and wetlands.

Surface water export of pesticides generally accounts for a small portion (<1%) of the dissipation/degradation pathways for pesticides applied to cropland. Consequently, the losses of these compounds by surface water runoff are seldom of consequence to farmers.

2.3. HIERARCHICAL ASPECTS OF AGRICULTURAL POLLUTION

Many of the characteristics of agricultural nonpoint pollution, as it affects both ambient stream water quality and pollutant loading, are greatly influenced by the size of the watershed under investigation. The importance of these "scale" or "hierarchical" effects is readily apparent in the Lake Erie Basin studies, which include watersheds ranging in size from 11.3 to 16,395 sq km. Many of these scale effects are a consequence of the routing of water from various portions of the watershed through drainage networks, with the attendant mixing of water from differing portions of storm hydrographs. Other characteristics relate to an "averaging" effect on "inputs" that occurs within large watersheds. Still other characteristics reflect the increasing role of in-stream processing as watershed size increases.

Some of the important hierarchical effects observed for nonpoint source pollutants in these studies are:

1. Peak pollutant concentrations are higher in the runoff from small watersheds than in the runoff from large watersheds. This effect is most pronounced for sediments and sediment associated pollutants but is also evident in soluble pollutants, including nitrates and pesticides.

2. The duration of exposures to pollutants is much longer in streams with large watersheds than in streams with small watersheds. Small streams "clear up" much more quickly than large streams.

3. As a consequence of 1 and 2 (above), the exposure patterns in small streams tend toward "acute" episodes, while the exposures in large streams tend toward "chronic" patterns. Whether such exposures actually have acute or chronic effects depends on the actual concentrations of specific pesticides and the composition of the biological community. Since the biological communities of small streams differ from those of large streams, assessment of ecological impacts must consider the exposure patterns likely to be encountered by a particular community.

4. The annual variability in material export is greater in small watersheds than in large watersheds. This effect is probably associated with less averaging of extreme (and low recurrence) rainfall events in small watersheds. Since annual variability in agricultural runoff is large in any case, the larger amount of annual variability in the outputs of small watersheds makes the task of evaluating the effectiveness of agricultural pollution abatement demonstration projects particularly difficult. Such projects tend to focus on small watersheds where significant changes in management practices can more easily be achieved. The short planning horizon for such projects generally results in inadequate baseline data for pre-treatment conditions and inadequate follow-up studies for post project assessment.

5. As watershed size becomes smaller, increasing proportions of the total annual export of pollutants occurs in decreasing proportions of time. However, the high rates of export from small watersheds are distributed into larger numbers of individual events. Consequently, it takes more sampling effort to accurately measure the output of a small watershed than the output of a large watershed. Since high export rates occupy less time in a small watershed, it is easier to "miss" them in a sampling program.

6. In small watersheds, the dominant season of sediment export corresponds to the dominant season of erosion on the landscape, i.e., in the late spring/early summer period, when there is a combination of high intensity rainfall events and low amounts of ground cover. In large watersheds, the dominant period of sediment export occurs in the late winter/early spring, during the periods of peak discharge. During these large events in large rivers, sediment previously deposited in the channel system is resuspended and exported.

7. While watershed size affects seasonal export of sediments and particulate associated pollutants, the seasonal export of soluble pollutants, such as soluble phosphorus, nitrate, and soluble pesticides, is not affected by watershed size. Winter is the dominant season for the export of soluble phosphorus, and winter and spring are the dominant seasons for nitrate export, while pesticide export is largely confined to the late spring/early summer periods.

SECTION 3

RECOMMENDATIONS

3.1. LAKE ERIE BASIN AGRICULTURAL POLLUTION ABATEMENT PROGRAMS

3.1.1. Comprehensive Agricultural Pollution Abatement Programs Are Needed

While much of the early emphasis of agricultural pollution abatement demonstration studies in the Lake Erie Basin focused on phosphorus load reduction, it has become clear from the monitoring projects that agricultural runoff affects many aspects of regional water quality. Consequently, programs which address sediment, particulate phosphorus, soluble phosphorus, nitrate, and pesticides are in order. Such programs, in fact, represent the trend which has occurred within the Lake Erie demonstration projects. Because of the major off-site damages associated with cropland erosion, conservation tillage should continue to be an integral part of such programs. Conservation tillage represents effective means to reduce loading of both sediment and particulate phosphorus. More attention will need to be focused on fertilizer and pesticide issues, as well as crop rotation patterns.

Fortunately, comprehensive programs are likely to help improve the economic condition of area farmers, rather than cause additional economic burden. A key to the economic recovery of farmers will be more careful management of the fuel, fertilizer, and pesticide inputs and of the soil resource base necessary to achieve realistic and economic yields. Reducing the overapplication of fertilizers and pesticides will also reduce their runoff into waterways or percolation into groundwater. Given the magnitude of the off-site damages currently associated with the essential human enterprise of food production, it is in the public's interest to aid farmers in becoming better managers. Such aid can be channeled through the existing infrastructure of the Extension Service, the Soil and Water Conservation Districts, and the Soil Conservation Service. More research on "low input, sustainable" agriculture at land grant universities would also be appropriate. Since, in the long run, the economic recovery of the agribusiness community also hinges on the competitiveness of U.S. farmers, it is in the best long term interests of the agribusiness community to help farmers reduce their fertilizer and pesticide inputs to the minimum necessary for maintaining adequate yields within the context of conservation farming systems.

3.1.2. Multi-media Aspects of Agricultural Pollution Must Be Considered

Agricultural pollution abatement programs aimed at reducing surface water contamination should not aggravate groundwater contamination problems and vice versa. Furthermore, the significance of volatization of agricultural chemicals, coupled with atmospheric transport, should be considered.

3.1.3. The Concept of Targetting Needs To Be Expanded within the Context of the Multi-pollutant, Multi-media Characteristics of Agricultural Nonpoint Pollution

The broad range of both particulate and soluble pollutants from cropland runoff necessitates a re-evaluation of the concept of "targetting". Targetting to areas of high gross erosion would certainly not be appropriate for addressing the problems of nitrate and pesticide runoff. Nor would such targetting efficiently address the problems of wintertime soluble phosphorus export. In fact, targetting to areas of highest gross erosion may not even be the most effective way to reduce sediment yields at the mouths of the major rivers emptying into Lake Erie. Targetting must also consider the potential for groundwater contamination. More research is needed on the sources, transport, fates, and effects of various types of pollutants as they move from the land to and through stream systems and /or into groundwater. Such research will support more effective targetting, and thereby increase the efficiency of agricultural nonpoint source control programs.

3.1.4. Farmer Education Programs Related to Agricultural Nonpoint Pollution

While many farmers are aware that agricultural practices can affect water quality, few are aware of the multi-pollutant, multi-media aspects of the problem as it occurs in their local region. The extensive local data now available for Lake Erie tributaries, and for regional groundwater, need to be effectively relayed to the farming community and to the local agribusinesses and government agencies which support this community. Given a detailed awareness of the problems, as they occur "in their own backyard", they will be much more amenable to considering modifications of their farming practices that will reduce agricultural pollution. Just as the extension service has carried the results of agronomic research to individual farmers, an environmental extension effort needs to be mounted to carry the results of environmental research to individual farmers. Since nonpoint pollution problems stem from the cumulative effects of many small sources, the related educational efforts need to reach out to the grassroots level.

3.2. RESEARCH ON AGRICULTURAL NONPOINT POLLUTION IN THE LAKE ERIE BASIN

3.2.1. Long Term, Large Scale Studies Are Needed for Model Verification

It is within the context of large scale, long term studies of agricultural nonpoint pollution that the adverse impacts of food production on regional water resources become apparent. It is within this same context that the effectiveness of measures aimed at reducing these adverse impacts must be verified. While models based on the effects of "best management practices", as applied within research plots and individual fields, are useful in predicting the responses of larger systems to such practices, model predictions should not be equated with "real world" verification. Ideally and realistically, such model predictions do need to be validated at the scale to which they are being extrapolated.

Since the achievement of a high level of adoption of best management practices in large watersheds will take a long time, long term studies are essential. An ecosystem approach, in which as many of the significant input and output variables as possible are measured, will be necessary to support assessment of system responses to management efforts and to verify the predictions of modeling approaches to nonpoint pollution control. While the complexity and costs of such research are high, it is essential that environmental degradation associated with food production be minimized. A network of large scale, long term agro-ecosystem studies should be established, including sites within major physiographic regions. The paucity of such studies is evident from the lack of data with which to compare the results of the Lake Erie Basin studies. The lack of data with which to assess the national scope of groundwater contamination from agricultural activities further reflects our ignorance of fundamental relationships between food production and water resources.

3.2.2. Future Directions for the Lake Erie Agro-ecosystem Program

Heretofore agricultural nonpoint pollution research in the Lake Erie Basin has consisted of the collection of many parts, somewhat akin to collecting the pieces of a puzzle. Considerable input and output data for the watersheds have been collected. The adequacy of various stream sampling programs has been evaluated. Techniques for efficiently collecting the data and analyzing the resulting volumes of information have been developed. Numerous demonstration programs have educated the agricultural "infrastructure" (i.e., the Extension Service, the Soil Conservation Service, Soil and Water Conservation District personnel, Agricultural Stabilization and Conservation Service employees, and agricultural chemical dealers) on the advantages of conservation tillage, as well as several pitfalls to avoid when using this technology.

A major need is to advance the integration of all the data and programs underway in the Lake Erie Basin. Such integration can be accomplished by adopting an ecosystem approach for the agricultural watersheds draining into Lake Erie. This approach is described in Section 4 of this report, as the Lake Erie Agro-ecosystem Program. Some of the specific research issues that need to be addressed within that program are:

1. Analyses should be initiated on the relationships between the input variables, both management-related and weather-related, and the output variables. An ability to separate weather induced variations in material export from changes associated with changing management practices is a fundamental requirement for assessing the effectiveness of various practices in reducing agricultural pollution. Furthermore, any trends associated with climatic changes will need to be distinguished from responses to changing management practices.

2. Where possible, several watersheds should be selected where special BMP implementation efforts will be coordinated with appropriate monitoring of both weather inputs and stream outputs. Such special watershed studies can serve as sites for model development, calibration, and verification, and for support of more rapid assessment of the effects of control programs.

3. The "output" studies should be expanded to include assessments of changing agricultural practices on stream communities. While we bemoan the lack of historical data upon which to judge the impacts of current agricultural practices on stream communities, we have probably not adequately characterized current stream communities in such a way as to facilitate assessment of the effects of changing or future agricultural practices.

4. The interfaces between the agricultural ecosystems and the Lake Erie ecosystem, ie., the lower sections of rivers, and their associated wetlands and bays, need additional study if we are to better manage the entire system. The transport and processing of materials within the interface zones between the lake and the land constitute a highly complex area.

SECTION 4

BACKGROUND OF THE LAKE ERIE AGRICULTURAL NONPOINT POLLUTION RESEARCH AND DEMONSTRATION PROGRAMS

4.1. NONPOINT SOURCE POLLUTION STUDIES IN THE GREAT LAKES AND LAKE ERIE BASINS

In the Great Lakes Basin, and especially in the Lake Erie Basin, nonpoint sources of pollution have received particularly detailed study. Through a series of U.S.-Canadian investigations coordinated by the International Joint Commission's Pollution from Land Use Activities Reference Group (PLUARG), a comprehensive overview of nonpoint source pollution in the Great Lakes was developed in the late 1970's (International Joint Commission 1978b, 1980, 1983). These studies revealed that land use activities do adversely impact Great Lakes water quality. Agricultural land use was singled out as a major source of sediments, nutrients and pesticides impacting several regions, including Green Bay, Saginaw Bay and much of the western and central basins of Lake Erie. These studies indicated that, although the land area draining into Lake Erie occupies only 11.5% of the total land area in the Great Lakes Basin, Lake Erie tributaries carried 58% of the total tributary suspended solids load entering the Great Lakes (International Joint Commission 1978b). Maps of unit area phosphorus yields for the Great Lakes indicated that the largest aggregation of lands with high unit area phosphorus yields occurs within the watersheds draining into the western and central basins of Lake Erie (International Joint Commission 1978b). These high sediment and phosphorus losses are associated with the intensive row crop agriculture which dominates land use in large portions of the Lake Erie Basin. Consequently, agricultural nonpoint pollution has been studied most extensively in the Lake Erie Basin.

Much of the detailed study in the Lake Erie Basin was conducted as part of the U.S. Army Corps of Engineers' Lake Erie Wastewater Management Study (LEWMS) (U.S. Army Corps of Engineers 1982). That study included the development of a detailed geographical information system for the entire United States portion of the Lake Erie Basin (Adams et al. 1982) as well as detailed water quality studies (Baker 1984, 1985 a,b). The LEWMS program was coordinated with both the PLUARG studies and the Areawide Waste Treatment Management planning studies conducted under Section 208 of the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500).

By linking together support from a series of planning and research grants, the Water Quality Laboratory at Heidelberg College has been able to develop a combination of detailed and long term studies of the impacts of agricultural runoff on regional water quality that are unique. During the course of these studies, major financial support has come from: the Army Corps of Engineers; the U.S. EPA (several offices); the State of Ohio; the Toledo Metropolitan Area Council of Governments; the cities of Tiffin, Upper Sandusky and Bucyrus; private foundations, including the Rockefeller Foundation, the Joyce Foundation and the Gund Foundation; and industries, including soap and detergent manufacturers, pesticide manufacturers and power companies.

The resulting data have been used extensively for a wide variety of purposes. The

International Joint Commission uses these data to calculate phosphorus loading from tributaries into Lake Erie. The data have been used extensively in major planning studies for this region including "208" planning of the Toledo Metropolitan Area Council of Governments, the Ohio Environment[illegible]tection Agency and in the U.S. Army Corps of Engineers' Lake Erie Wastewater Management Study (U.S. Army Corps of Engineers 1982). Several studies aimed at developing nonpoint source models (Cahill et al. 1979, Zison 1980), and river transport models (Verhoff et al. 1978), have also used these data sets. The data sets have also been used to evaluate sampling and calculational strategies for load estimation (Richards and Holloway 1987, Watson 1985) and for developing techniques to characterize ambient water quality impacts of agricultural runoff (Shelly 1986).

Since the data so clearly illustrate many of the charcteristics of agricultural nonpoint pollution, the Water Quality Laboratory is increasingly called upon to participate in and /or present workshops at the local, state and national level on the topics of agricultural pollution. Recent presentations have been made to: the National Alliance of Independent Crop Consultants, the American Fisheries Society, the American Association of County Agricultural Agents, U.S. EPA--Office of Pesticide Programs, the National Federation of Soil and Water Conservation Districts, the National Association of State Departments of Agriculture, the National Agricultural Chemicals Association, and the National Association of Conservation Districts.

4.2. AGRICULTURAL POLLUTION ABATEMENT DEMONSTRATION PROGRAMS

As it became evident in the above studies that agriculture was a major source of phosphorus entering Lake Erie, ways to reduce agricultural phosphorus loading were examined. Because most of the phosphorus delivered to Lake Erie is associated with sediment, erosion control measures which should reduce sediment transport provide a means to reduce phosphorus loading to the lake. A demonstration project in the Black Creek watershed of Allen County, Indiana (Lake and Morrison 1977) suggested that erosion control through structural measures would be an extremely costly method to reduce phosphorus loading to Lake Erie. Instead of structural measures, conservation tillage was identified as a potentially effective means of reducing erosion and the associated suspended sediment and particulate phosphorus loadings into Lake Erie. Conservation tillage consists of a variety of techniques which increase crop resides on the soil surface thereby reducing erosion (See special issue of the Journal of Soil and Water Conservation, Volume 38, May-June 1983 for an overview of conservation tillage.)

The agronomic suitability of various types of conservation tillage for Lake Erie Basin soils was then evaluated in a series of demonstration studies. The first of these demonstrations was located in the Honey Creek Watershed of the Sandusky River Basin as part of the LEWMS study. The success of the Honey Creek Demonstration Project (Honey Creek Joint Board of Supervisors 1982) led to U.S. EPA-supported conservation tillage demonstration programs in Allen and Defiance counties of Ohio and eventually to programs in 31 counties of the Lake Erie Basin (Morrison 1984). The major objectives of these demonstration studies were to acquaint as many farmers as possible with conservation tillage techniques, to develop local data comparing conventional tillage and conservation tillage in terms of crop yields and production costs, and indirectly to accelerate area-wide adoption of conservation tillage. These demonstration projects have confirmed that, for many Lake Erie Basin soils, conservation tillage can provide either equivalent or increased profits in comparison with conventional tillage (Conservation Tillage Information Center 1985).

In 1983, through a Supplement to Annex 3 of the Great Lakes Water Quality Agreement of 1978, the U.S. and Canada agreed to reduce phosphorus loading to Lake Erie by an additional 2,000 metric tons per year beyond the reductions achievable by reducing major municipal point source phosphorus loading to 1 mg/L P in the effluents. The U.S. phosphorus reduction strategy (Great Lakes Phosphorus Task Force 1985), as well as those of the individual states (e.g., see Ohio EPA 1985), is focusing on conservation tillage as a major tool to reduce phosphorus loading to the lake. Implementation of agricultural phosphorus load reduction programs should consequently consist of continuing and /or expanding programs to aid farmers in adopting conservation tillage.

While much of the initial emphasis of the Lake Erie agricultural pollution abatement demonstration programs focused on tillage practices to reduce sediment and particulate phosphorus loading, the scope of the programs has significantly broadened. The tributary monitoring program pointed out that unexpectedly large proportions of nitrogen fertilizers applied by farmers were not incorporated by crops but instead were being exported to Lake Erie and were affecting public water supplies derived from tributaries. Furthermore numerous herbicides applied to cropland are present in area rivers and pass through conventional water treatment plants with little attenuation (Baker 1983d). At the same time the input costs for crop production were rising and the market value of crops was decreasing, placing many farmers in serious economic difficulties. These factors have led to the growth of programs which link increased farm profits with reductions in agricultural pollution through improved management of not only tillage, but also of fertilizer and pesticide inputs.

4.3. POSSIBLE WATER QUALITY TRADE-OFFS WITH CONSERVATION TILLAGE

The primary water quality benefits of conservation tillage fall in the area of reduced soil erosion and an accompanying reduction in sediment and particulate phosphorus export from agricultural watersheds. The proportional reduction in watershed sediment export may differ considerably from the proportional reduction in gross erosion rates within the watershed, depending on the relative sediment delivery ratios from treated and untreated areas. To the extent that the concept of stream sediment carrying capacity applies to the transport of clay fractions in Lake Erie tributaries, reductions in gross erosion on the landscape may be accompanied by increased stream bank and stream bed erosion rates, thereby diminishing hoped-for reductions in sediment transport. However, the sediment derived from stream banks would not carry the same load of agricultural nutrients or pesticides as sediment derived from cropland. Furthermore, it is unclear how soon reduced erosion of the landscape would become evident as reduced sediment yields since the time of transit of sediment from fields to and through stream channels to Lake Erie is uncertain. Therefore, the magnitude of sediment yield reductions that will actually accompany cropland erosion control measures in the Lake Erie Basin remains to be determined.

The extent of reduction in particulate phosphorus loading that will accompany erosion control programs is uncertain due to all of the uncertainties noted above regarding the extent of sediment reductions. Additional uncertainties are introduced due to probable changes in average particle size of the exported sediment. It is likely that the average particle size will decrease as a result of erosion control programs. It is expected that this will be accompanied by an increase in the phosphorus to sediment ratio thereby making the proportional reductions in phosphorus loading less than the proportional reductions in sediment loads (U.S. Army Corps of Engineers 1982).

While the erosion reduction benefits of conservation tillage are well documented, at least at the level of plot and field-sized studies, much concern exists regarding the possibility that conservation tillage could aggravate other water quality problems, especially the contamination of surface and groundwater by nitrates and pesticides (Crosson 1981; Hinkle 1983).

Nitrate and many currently-used pesticides are primarily transported as dissolved materials in water rather than as adsorbed materials on sediments. In addition, soluble forms of phosphorus are much more bioavailable than particulate phosphorus. Data from plot studies have frequently shown that conservation tillage increased runoff amounts and /or concentrations of nitrates and soluble phosphorus (Baker & Laflen 1983; Crosson 1981). In a review of the effects of conservation tillage on pesticide use and runoff losses, Logan (1981) concluded that pesticide losses would not be expected to change measurably with a shift to conservation tillage. In part, Logan's conclusions were based on evidence that for the soil types in northwestern Ohio, conservation tillage would do little to increase water infiltration into soil and thus decrease surface runoff (Logan and Adams 1981). Since herbicides move into streams as part of the surface runoff from fields, if surface runoff is not significantly reduced, export of soluble pesticides is also unlikely to be reduced. If application rates of soluble herbicides increase with conservation tillage, it is likely that herbicide concentrations in surface waters will increase. However, in conservation tillage demonstration projects in the Lake Erie Basin, soluble herbicide application rates have shown little or no increase. The effects of conservation tillage on the movement of nitrates and pesticides into groundwater or surface water was the subject of an EPA-sponsored conference in Chicago in 1986. The proceedings were published in early 1987 (Logan et al. 1987).

4.4. THE LAKE ERIE AGRO-ECOSYSTEM PROGRAM

The combination of extensive baseline data and forthcoming changes in agricultural practices, resulting from either agricultural nonpoint pollution control programs or economic considerations, presents important opportunities to advance the science of agricultural nonpoint pollution control through a continuation and expansion of programs in the Lake Erie Basin. To efficiently address the complex research issues that are involved, current programs are being advanced within the context of a large scale, long term agricultural ecosystem program (Figure 4.1).

Agricultural nonpoint source pollution reflects what ecologists have referred to as the "leakiness" of agricultural ecosystems (Odum 1969). Relative to natural ecosystems, cultivated ecosystems have a high potential for erosion and nutrient losses (Woodmansee 1984). Many of the "best management practices" aimed at reducing agricultural nonpoint pollution attempt to "tighten up" the nutrient cycles of these agricultural ecosystems and confer upon these systems more of the characteristics of natural ecosystems, such as persistence and stability. Farmers are being urged to adopt a "systems approach" to production which involves careful management of fertilizers and pesticides, as well as plant residues (Pierce 1985). Concepts of "low input, sustainable" agriculture are receiving increased attention.

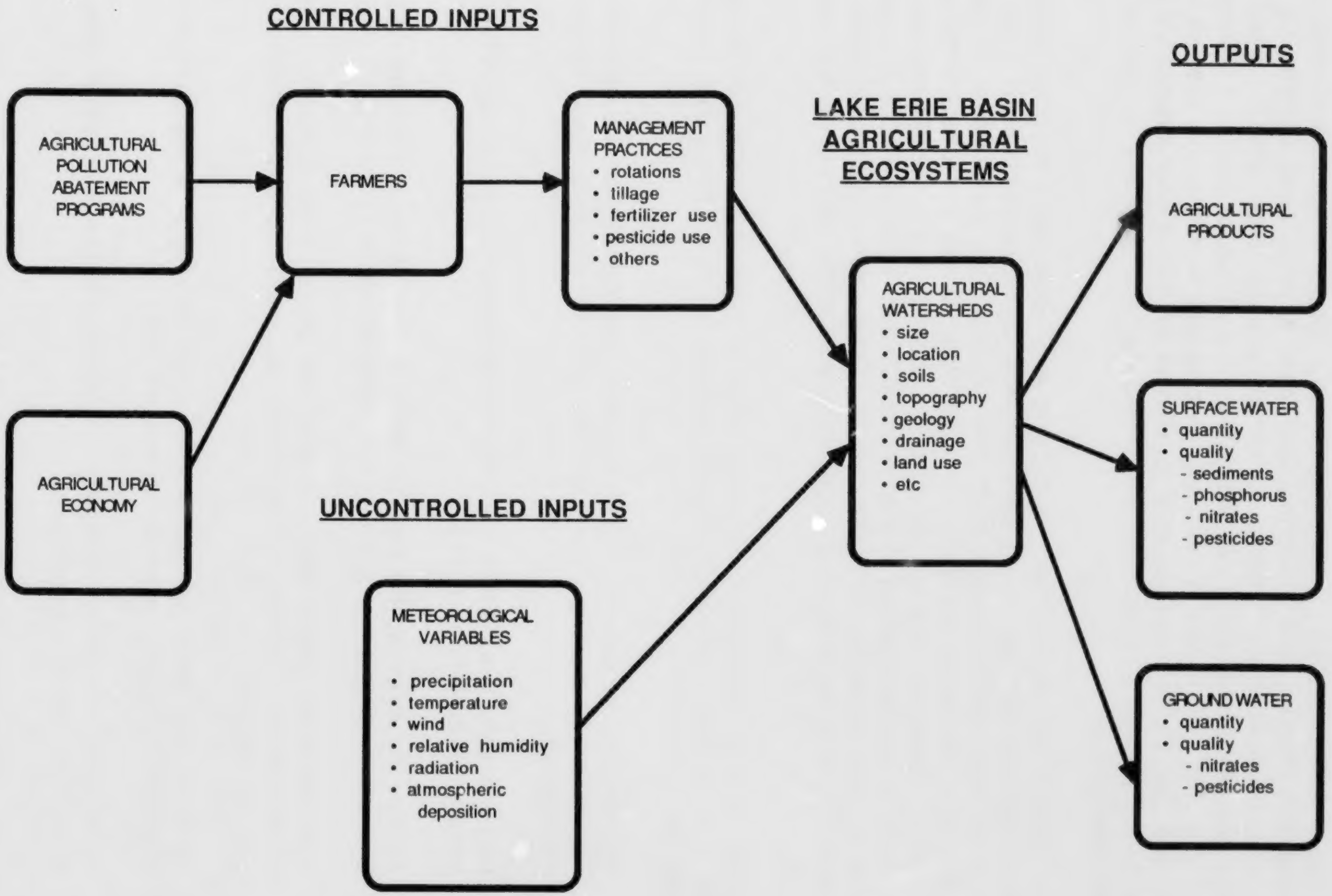

CONTROLLED INPUTS
AGRICULTURAL POLLUTION ABATEMENT PROGRAMS
FARMERS
AGRICULTURAL ECONOMY
MANAGEMENT PRACTICES
• rotations
• tillage
• fertilizer use
• pesticide use
• others
UNCONTROLLED INPUTS
METEOROLOGICAL VARIABLES
• precipitation
• temperature
• wind
• relative humidity
• radiation
• atmospheric deposition
LAKE ERIE BASIN AGRICULTURAL ECOSYSTEMS
AGRICULTURAL WATERSHEDS
• size
• location
• soils
• topography
• geology
• drainage
• land use
• etc
OUTPUTS
AGRICULTURAL PRODUCTS
SURFACE WATER
• quantity
• quality
- sediments
- phosphorus
- nitrates
- pesticides
GROUND WATER
• quantity
• quality
- nitrates
- pesticides

Figure 4.1. Major components and their relationships for agro-ecosystem studies

While management practices reflect "controllable" inputs to agricultural ecosystems, weather conditions reflect a major "uncontrollable" input, to which these systems are highly sensitive. Annual variability in weather conditions causes large annual variability in nutrient and sediment export which can easily mask the effects of improved management practices in reducing such export. A major task in programs to assess the effectiveness of agricultural pollution abatement practices is to account for the weather induced variability. Consequently, it is necessary to measure both the management inputs and the weather inputs for the study watersheds.

For the management of the Great Lakes Basin as a whole, there is strong support for utilizing an Ecosystem Approach which addresses "the interacting components of air, land, water and living organisms, including man" (International Joint Commission 1978a). In fact, this approach was recommended in the 1978 Water Quality Agreement (International Joint Commission 1978a). An important aspect of this approach is the use of mass balance in the management of both conventional and persistent pollutants (U.S. EPA 1985b). The same rationale that suggests an ecosystem approach for the Great Lakes Basin is also applicable to subcomponents of the Basin, such as the agricultural ecosystems draining into the Lake Erie Basin.

The generalized agro-ecosystem model, as shown in Figure 4.1, does facilitate efficient approaches to the multiple objectives associated with this program. These objectives include the provision of:

1. accurate data on pollutant loading into the Lower Great Lakes to support the application of mass balance approaches to Great Lakes water quality management,
2. baseline data upon which to evaluate the effectiveness of agricultural pollution abatement measures,
3. site-specific water quality data to help garner local support among rural and urban residents for agricultural pollution abatement programs,
4. sufficient water quality data to support the development, calibration and verification of agricultural runoff models, as applied to large watersheds and river basins,
5. water quality data sets to support evaluation of tributary sampling strategies and loading calculation techniques, and
6. techniques for tracking agricultural management practices within large tillage demonstration watersheds.

A Prospectus for the Lake Erie Agro-ecosystem Program has recently been prepared by staff of the Water Quality Laboratory at Heidelberg College and is available upon request.

4.5. RELATED STUDIES UNDERWAY AT THE HEIDELBERG COLLEGE WATER QUALITY LABORATORY

In addition to the ongoing tributary loading studies, as described in this report, several related studies are in progress. Most of these studies support the Lake Erie Agro-ecosystem Program.

4.5.1. Tillage Tracking Program

In order to gain a more precise estimate of tillage practices actually in use by farmers in the study watersheds, a windshield survey technique was developed and applied to the Honey Creek and Rock Creek watersheds. The technique includes recording a set of information twice per year on approximately 2000 individual fields. The results of the first three years of the program have recently been reported by Krieger (1986a). Similar data are available for each field in the Lost Creek Watershed.

4.5.2. Rural Drinking Water Studies

A program of groundwater studies, utilizing information from the analysis of water from private wells, was initiated in 1985. The program originally focused on "critical" areas, as judged by cooperating personnel from county health departments. While the study did result in the location of a few "hot spots" of nitrate contamination, even these hot spots had low, if any, pesticide contamination. Subsequently, the nitrate portion of the program was expanded to a much larger sampling of wells with no attempt to focus on critical areas. Of the initial 3,600 samples tested in that program, the nitrate-nitrogen concentrations in 83% of the wells were less than 0.3 mg/L. In only 2.6% of the wells was the concentration above the drinking water standard of 10 mg/L. The nitrate studies noted above are being expanded and an interim report on our groundwater studies will be prepared in November 1987.

4.5.3. Pesticide Studies in Rainwater

A study of the concentrations of currently used pesticides in rainwater was initiated in 1984. The study indicates that several herbicides are present in rainfall during the May, June and July periods. The pesticide concentrations are much higher in rainwater than in groundwater, although the rainfall concentrations are lower than in the rivers during the spring runoff events. The sampling program includes sites at West Lafayette, Indiana, at Potsdam, New York, at Parsons, West Virginia, and at Tiffin, Ohio. Results from the first two years of this study have recently been published (Richards et al. 1987).

4.5.4. Rainfall Network

To augment the existing network of NOAA weather stations, a cooperative network of daily rainfall stations was established in 1982. It involves approximately 120 local observers (mostly farmers) in the three counties that make up most of the Sandusky River Basin. From April through October, daily rainfall amounts are recorded and submitted at monthly intervals to our laboratory, where the data are entered into computer storage. The main purpose of the project is to obtain information for supporting trend analysis and modeling efforts in these watersheds.

In connection with this program, our laboratory operates the NOAA cooperative weather station for Tiffin, Ohio. This station includes a continuously recording raingauge, as well as a standard raingauge and temperature recording equipment. In 1987, an evaporation pan will be installed at this station. The lab also operates recording raingauges at other locations in the study watersheds.

4.5.5. Wetlands Research Programs

The laboratory is involved in research at the interface between the river systems and Lake Erie. Currently work is in progress under a Sea Grant award through Ohio State University to measure pesticide concentrations in wetlands adjacent to the lower portions of the Sandusky River and at the Old Woman Creek Nature Preserve.

4.5.6. Statistical Analysis of Tributary Sampling Programs

Under a research grant from the Great Lakes National Program Office the laboratory is evaluating various sampling strategies aimed at producing accurate loading data for Great Lakes tributaries. Both event response and stable response streams are under investigation. In event response streams, the concentrations of both particulate and dissolved pollutants from nonpoint sources increase during runoff events.

4.5.7. Pesticide Removal Research

The laboratory has a cooperative agreement with the U.S. EPA's Water Engineering Research Laboratory in Cincinnati, Ohio to evaluate the effectiveness of various treatment techniques for removing pesticides from drinking water. The techniques include carbon filtration, reverse osmosis, and ozonation. Results of this research, as it applies to alachlor removal have recently been summarized (Miltner et al. 1987).

4.5.8. Bioavailable Phosphorus Loading to Lake Erie

Beginning in 1982, additional phosphorus forms were analyzed on subsets of the tributary samples. These additional analyses included NaOH extractable phosphorus, which provides an estimate of the bioavailable particulate phosphorus fraction. In addition, the soluble hydrolyzable phosphorus fraction was measured. These two measurements allow calculation of bioavailable phosphorus loading to Lake Erie. A progress report on these studies was submitted to the Great Lakes National Program Office in 1983 (Baker 1983b). Data collected since that time will be included in the report summarizing the 1986 water year program. That report is currently in preparation.

SECTION 5

STUDY METHODS

5.1. SAMPLING LOCATIONS

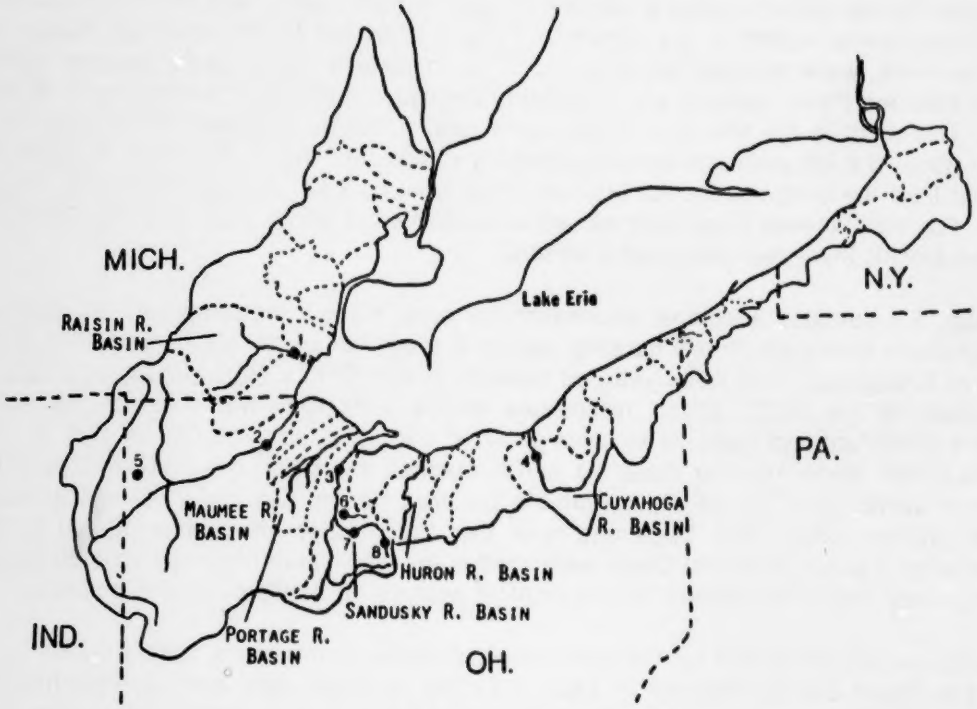
The sampling locations for Lake Erie tributaries are shown in Figure 5.1 and for Lake Ontario tributaries in Figure 5.2. All of the samples are collected either at or near U.S. Geological Survey stream gauging stations. These stations, along with their corresponding USGS identification numbers, are shown in Table 5.1. Except for the Maumee, Raisin and Genesee rivers, water samples are collected in the immediate vicinity of the gauging station. For the Maumee River; samples are collected at the water intake plant for the city of Bowling Green. This plant is the site of a USGS water quality monitor (Number 04193490) and is located about 3.2 km upstream from the gauging station. For the River Raisin, samples are collected from the bridge at the Ida-Maybee Road, about 1.3 km upstream from the gauging station. For the Genesee River samples are collected from a bridge located at the Rochester Gas and Electric Plant near the gauging station.

Table 5.1 contains additional information for each station, including: 1) the drainage area upstream from each stream gauging station; 2) the mean annual discharge for the period of record through the 1985 water year, as reported in the USGS's Water Resources Data for each state; 3) the USGS annual discharges for the 1982-1985 water years; and 4) the numbers of nutrient and pesticide samples analyzed each year as part of these studies. Data for Lost Creek are included in Table 5.1 and throughout this report even though this station has been funded as a part of grants from the Defiance County Soil and Water Conservation District (Baker 1986) and, beginning with the 1985 water year, from the U.S. Soil Conservation Service. The Lost Creek watershed is the smallest of the study watersheds and provides very useful information for hierarchical analysis of nonpoint source pollution.

Land use characteristics for the watersheds upstream from each sampling station in the Lake Erie Basin are summarized in Table 5.2. The land use data were derived from the geographical information system developed as part of the U.S. Army Corps of Engineers' Lake Erie Wastewater Management Study (U.S. Army Corps of Engineers, 1982). With the exception of the Cuyahoga River Basin, cropland dominates the land use within each watershed. The geographical information system has also been used for calculations of gross erosion for each watershed (Logan et al. 1982). Average gross erosion rates for each watershed are also listed in Table 5.2.

5.2. SAMPLING METHODS

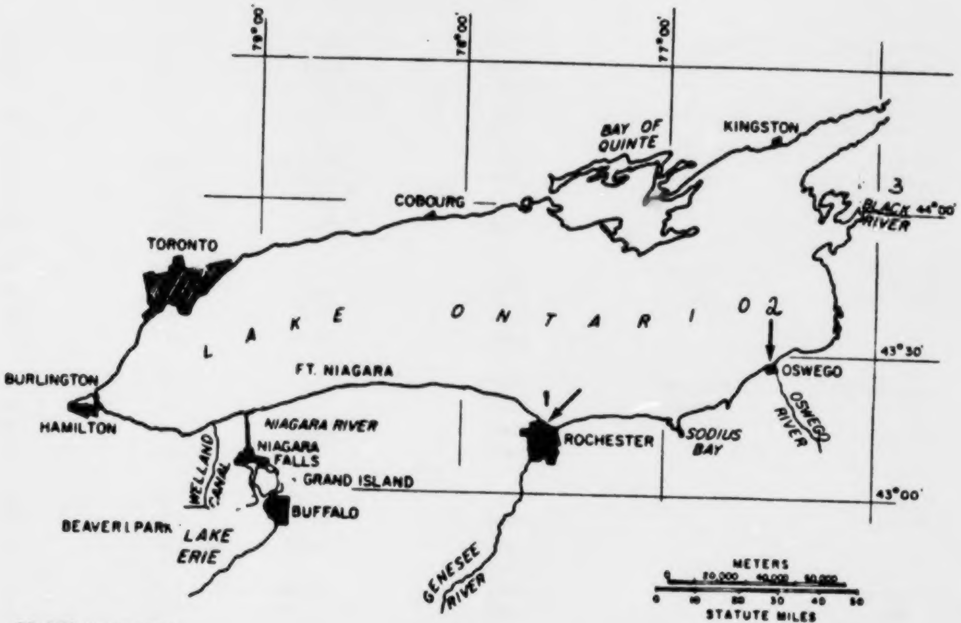
For all of the stations located in Ohio, automatic samplers (ISCO 1680 or equivalent) are used to collect discrete samples at 6 hour intervals, resulting in four samples per day which are collected at 0100, 0700, 1300 and 1900 hours. Each gauging station is equipped with an all-weather pumping system that operates continuously. The automatic samplers are housed in the gauging stations and the samplers pump water from sampling wells fed from the all weather pumps. For stations on smaller watersheds, such as Lost Creek, Rock Creek, and


MICH.
Lake Erie
N.Y.
RAISIN R. BASIN
PA.
MAUMEE R. BASIN
CUYAHOGA R. BASIN
HURON R. BASIN
SANDUSKY R. BASIN
IND.
PORTAGE R. BASIN
OH.
1
2
3
4
5
6
7
8

Sampling Locations:

1. River Raisin near Monroe, MI
2. Maumee R. at Bowling Green, OH water intake
3. Sandusky R. near Fremont, OH
4. Cuyahoga R. at Independence, OH
5. Lost Cr. tributary near Defiance, OH
6. Rock Cr. at Tiffin, OH
7. Honey Cr. at Melmore, OH
8. Upper Honey Cr. at New Washington, OH

Figure 5.1. Locations of the tributary monitoring stations in the Lake Erie Basin.


79°00'
78°00'
77°00'
BAY OF QUINTE
KINGSTON
3
BLACK RIVER
44°00'
COBOURG
TORONTO
LAKE ONTARIO
2
43°30'
OSWEGO
BURLINGTON
FT. NIAGARA
1
HAMILTON
NIAGARA RIVER
ROCHESTER
SODIUS BAY
OSWEGO RIVER
NIAGARA FALLS
WELLAND CANAL
GRAND ISLAND
43°00'
BUFFALO
BEAVER I PARK
LAKE ERIE
GENESEE RIVER
METERS
0
20,000
40,000
60,000
0
10
20
30
40
50
STATUTE MILES

SOURCE NOAA (1971)

Sampling Locations:

1. Genesee R. at Rochester, NY
2. Oswego R. at Oswego, NY
3. Black R. at Watertown, NY

Figure 5.2. Locations of the tributary monitoring stations in the Lake Ontario Basin.

Table 5.1. Listing of tributary monitoring stations, watershed areas, mean annual discharges, and, for the 1982-1985 water years, the water year discharges and the number of nutrient and pesticide samples analyzed.

Station USGS No.	Area Km^2 (Mean Annual Discharge, $10^6 m^3$)	Water Year	USGS Annual Discharge $10^6 m^3$	Samples Analyzed	
				Nutrients	Pesticides
Maumee R.	16,395 km^2	1982	7,107	479	53
01493500	(4,422)	1983	4,748	546	62
		1984	5,878	482	88
		1985	4,365	454	56
Sandusky R.	3,240 km^2	1982	1,390	469	51
04198000	(891.3)	1983	649.6	448	58
		1984	1,940	441	79
		1985	769.8	502	82
Cuyahoga R.	1,831 km^2	1982	919.8	447	24
04208000	(738)	1983	919.9	475	25
		1984	1,030	437	20
		1985	921.7	502	29
Raisin R.	2,699 km^2	1982	925.3	223	25
04176500	(650.2)	1983	874.4	312	32
		1984	753.0	313	43
		1985	816.7	310	31
Honey Cr.	386 km^2	1982	157.7	538	65
04197100	(124.1)	1983	88.72	514	68
		1984	168.2	483	100
		1985	91.43	480	121
Upper Honey Creek	44.0 km^2	1982	16.58	151	- -
	(15.36)	1983	11.06	416	58
04197020		1984	21.07	409	32
		1985	12.07	430	85
Rock Cr.	88.0 km^2	1983	- -	434	46
04197170		1984	43.13	522	87
		1985	19.83	540	143
Lost Creek Trib.	11.3 km^2	1982	6.799*	518	51
		1983	5.175*	784	51
04185440		1984	4.956*	399	57
		1985	4.840*	457	63
Genesee R.	6,390 km^2	1982	3,362.3	56	- -
04232000	(2,512)	1983	2,431.4	60	- -
		1984	3,826.4	43	- -
		1985	2,201.0	75	- -
Oswego R.	13,209 km^2	1982	6,715.1	52	- -
04249000	(5,991)	1983	5,085.3	60	- -
		1984	6,748.7	43	- -
		1985	4,682.1	75	- -
Black R. (NY)	4,854 km^2	1982	3,976	61	- -
04260500	(3,598)	1983	3,570	65	- -
		1984	4,295	62	- -
		1985	3,802	30	- -

* Discharge records subject to revision.

Table 5.2. Summary of land use and gross erosion rates for Lake Erie Basin tributary watersheds.

Watershed	Cropland %	Pasture %	Forest %	Water %	Other %	Gross Erosion Rate kg/ha/yr
Maumee R.	75.6	3.2	8.4	3.5	9.4	6,840
Sandusky R.	79.9	2.3	8.9	2.0	6.8	8,250
Cuyahoga R.	4.2	43.1	29.1	3.0	20.6	896.*
Raisin R.	67.1	6.8	9.0	3.0	14.1	9,750
Honey Cr.	82.6	0.6	10.0	0.5	6.3	6,860
Upper Honey Cr.	89.1	---	7.5	---	3.4	7,060
Rock Cr.	80.9	2.3	11.8	0.9	4.2	9,540
Lost Cr.	83.0	---	10.6	1.4	5.0	7,610.**

*This gross erosion rate was calculated using the normal cover factor for forested areas. Due to unusual combinations of soils and slopes in portions of the Cuyahoga River basin, erosion from this watershed area is much higher than the calculated value.

**This calculation was completed in 1987 by the U.S. Soil Conservation Service and includes the impacts of conservation tillage demonstration programs to increase residue levels on the soil.

Upper Honey Creek, a second sampler, set to collect samples at one or two hour intervals, is also used. The second sampler is either triggered automatically when the river stage reaches a certain level or is manually triggered during a runoff event. In either case, the time of sample collection is recorded on a printer. During low flow periods analyses are performed on only one sample per day. During storm events, as evidenced either by turbidity in the samples or by high stream discharges, all available samples are analyzed (four or more per day, depending on the station).

At the stations in Michigan and New York, grab samples are collected by local observers. For the River Raisin five samples per week are collected on a year-around basis. For the New York tributaries the local observers are instructed to collect at predetermined intervals (usually 2 per week) and to collect extra samples during high flow periods. In general, the sampling programs for the tributaries to Lake Ontario have been much less satisfactory than for the tributaries to Lake Erie, because local observers had to decide whether a particular storm event was a "large" event for a particular year, and because storms don't always come at convenient times.

Pesticide samples for Lake Erie Basin sampling stations are collected with automatic samplers at the Maumee River, Lost Creek, Sandusky River, Honey Creek, Upper Honey Creek and Rock Creek stations. For the Maumee and Sandusky rivers, ISCO Model 2100 samplers, containing 24 400 ml glass bottles, are used. In order to obtain sufficient volume of samples, two bottles are filled at each sampling time. Samples are collected twice per day. The capacity of each sampler is therefore two samples per day for six days. Since the samplers are serviced at weekly intervals, no samples are collected on the day preceeding sample pick-up.

Beginning in 1984 for Honey Creek and Rock Creek, in 1985 for Upper Honey Creek and in 1986 for Lost Creek, modified ISCO Model 1840 samplers were installed which pump directly into one-quart Mason jars. Since each sampler has 28 positions, these samplers allow collection of 4 samples per day for 7 consecutive days. Prior to the above dates, ISCO Model 2100 samplers were used, as described above, for sample collection at these smaller watersheds . At the Cuyahoga and Raisin river stations, pesticide samples are collected by grab sampling techniques. Samples for pesticide analyses are not collected from the Lake Ontario tributaries.

5.3. ANALYTICAL PROGRAM: NUTRIENTS, SEDIMENTS, AND CONDUCTIVITY

All samples are analyzed for soluble reactive phosphorus (SRP), total phosphorus (TP), suspended solids (SS), nitrate plus nitrite-nitrogen (NO23-N), total Kjeldahl nitrogen (TKN), ammonia (NH3), dissolved silica (Si02), chloride (Cl), and conductivity (Cond.). In the case of nitrate plus nitrite-nitrogen most of the nitrogen present in these rivers is in the form of dissolved nitrate. Throughout the text the term "nitrate" is used interchangeably with the abbreviation NO23-N.

The analytical methods are identified in Table 5.3 and have been described in detail in quality assurance materials submitted to the Quality Assurance Office, Region V, U.S. EPA. The following documents contain information on analytical methods and related quality control results:

1. Baker, David B. January 1981. "Quality Assurance Program for Detailed Tributary Loading Studies in Event Response Rivers." Submitted to James H. Adams, Chief, Quality Assurance Office, Region V, U.S. EPA.

2. Baker, David B. March 1982. "The Effects of Sample Storage for One Week Without Preservation on Soluble Reactive Phosphorus Loading Measurements." Submitted to David Payne, Quality Assurance Office, Region V, U.S. EPA and Marcella Gewirth, Great Lakes National Program Office, Region V, U.S. EPA.

3. Baker, David B. June 1982. Quality Assurance Program Update - Responses to the April 16, 1982 Report by the Region V, EPA Quality Assurance Office on its On-Site Evaluation of the Water Quality Laboratory of Heidelberg College, Tiffin, Ohio. Submitted to the Quality Assurance Office, Region V, U.S. EPA.

All of the nutrient analyses are done using Technicon Autoanalyzer II systems equipped with digital printers. The printed outputs for each analytical tray, including the environmental samples and the associated blanks, standards, and spikes, are transferred to computer storage. Thus, the performance of the analytical system at the time any particular sample was analyzed can be readily determined.

Table 5.3. Analytical methods used for nutrients and sediments.

Parameter	Abbreviation	STORET Number	Method[1]
Suspended Solids	SS	00530	Method 160.2 Non-Filterable, Gravimetric pp. 160.2-1 - 160.2-3
Total Phosphorus	TP	00665	Method 365.3 Colorimetric, Automated Ascorbic Acid Reduction, Two-Reagent (modified, EPA approved) Sulfuric Acid - Persulfate Digestion pp. 365.3-1 - 365.3-3
Soluble Reactive Phosphorus	SRP	00671	Method 365.3 Colorimetric, Automated Ascorbic Acid Reduction, Two-Reagent (modified, EPA approved) pp. 365.3-1 - 365.3-3
Nitrate + Nitrite-Nitrogen	NO23-N	00631	Method 353.2 Colorimetric, Automated Cadmium Reduction (dissolved) pp. 353.2-1 - 353.2-7
Ammonia Nitrogen		00608	Method 350.1 Colorimetric, Automated Phenate pp. 350.1-1 - 350.1-6
Total Kjeldahl Nitrogen	TKN	00625	Method 351.2 Colorimetric, Semi-Automated Block Digester, Automated Phenate pp. 351.2-1 - 351.2-5
Chloride	Cl	00940	Method 352.2 Colorimetric, Automated Ferricyanide pp. 325.2-1 - 325.2-3
Silica	SiO2	00955	Method 370.1 Colorimetric, Automated Molybdate pp. 370.1-1 - 370.1-5
Conductivity	Cond.	00095	Method 120.1 Direct Reading, Temperature Compensating. Probe pp. 120.1-1

[1] All methods are taken from the following reference: Methods for Analysis of Water and Wastes, U.S. Environmental Protection Agency, Monitoring and Support Laboratory, Cincinnati, Ohio 45268. EPA 600/4-79-020. 1979.

5.4. ANALYTICAL PROGRAM: PESTICIDES

Samples are analyzed for the pesticides listed in Table 5.4. The analytical procedures and related quality control program have been described in detail by Kramer and Baker (1985). The procedure involves methylene chloride extraction followed by Kuderna-Danish concentration, transfer to iso-octane and analysis by capillary gas chromatography using nitrogen-phosphorus thermionic detectors. By using a DB-1 and a DB-5 column, simultaneous confirmation is obtained for every sample on 14 out of the 18 compounds for which the system is routinely calibrated. Azobenzene is added to each extract to provide a marker for calculation of relative retention times. Representative chromatographs for a standard solution and the associated data system outputs are shown in Figure 5.3. In 1982 the analytical system consisted of a Varian Model 3700 system interfaced to a Spectra Physics Data System. In 1984 the system was upgraded to a Varian Model 3400 Gas Chromatograph interfaced with a Varian Vista Model 402 data system. Both systems are equipped with autosamplers. The data systems are linked directly to the WQL's VAX 11/750 computer. The reports, as shown in Figures 5.3b and c, are transferred directly into the laboratory computer.

The quality control program includes the analysis of spiked samples, blanks, and replicates, as well as an interlaboratory sample exchange program with several pesticide manufacturers. Detection limits, mean percent recoveries and linear ranges for the most commonly observed pesticides are shown in Table 5.5. Linear ranges were determined by analysis of a dilution series of mixed standards. The sample exchange program indicated that correction of WQL pesticide data for recoveries less than 100%, using the mean percent recoveries, results in values that agree closely with those of the pesticide manufacturers. In this report data presented in summary tables have been corrected for recoveries less than 100% where indicated using the percent recoveries shown in Table 5.5. The pesticide data in Appendix II have not been corrected for recoveries less than 100%.

Table 5.4. Pesticides identified on each channel of the gas chromatograph and representative retention times.

DB5 Column (Channel 1)			DB1 Column (Channel 2)		
Peak #	Time	Name	Peak #	Time	Name
1	21.74	EPTC	1	20.17	EPTC
2	25.56	Butylate	2	24.13	Butylate
3	35.59	Azobenzene	3	33.23	Azobenzene
4	36.22	Ethoprop	4	33.49	Ethoprop
5	38.54	Trifluralin	5	36.33	Phorate
6	39.17	Phorate	6	36.68	Trifluralin
7	41.36	Simazine	7	37.81	Carbofuran
8	41.64	Carbofuran	8	37.97	Simazine
9	41.89	Atrazine	9	38.65	Atrazine
10	43.15	Terbufos	10	40.43	Fono/Terb$^+$
11	43.36	Fonofos	11	44.02	Metribuzin
12	43.95	Diazinon	12	46.27	Alachlor
13	47.88	Metribuzin	13	48.48	Cyanazine
14	49.18	Alachlor	14	49.50	Metolachlor
15	51.17	Linuron	15	52.35	Pendimethalin
16	52.36	Metolachlor			
17	53.02	Cyanazine			
18	55.61	Pendimethalin			

$^+$Fonofos and terbufos are not separated by this column under these operating conditions.

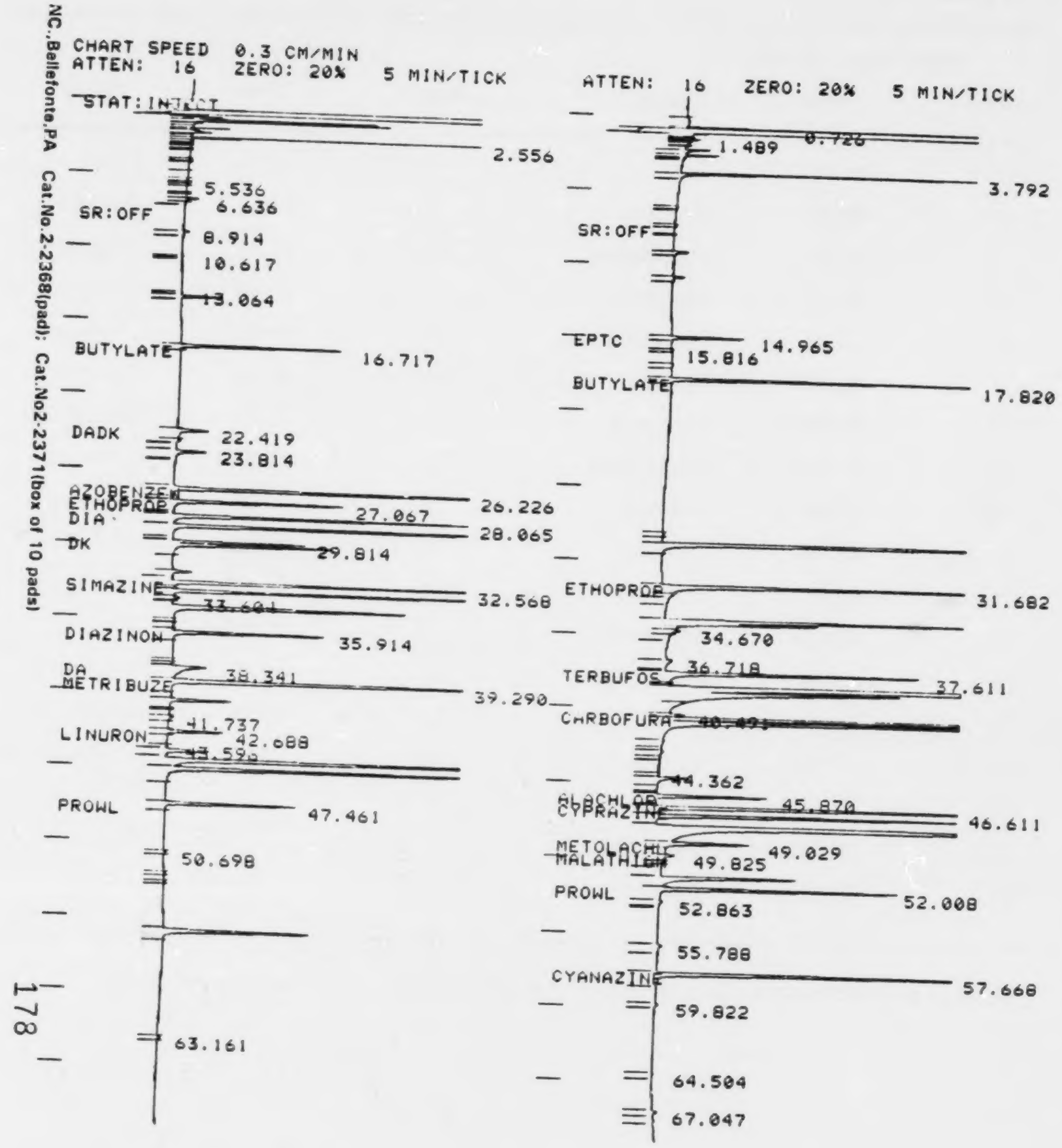
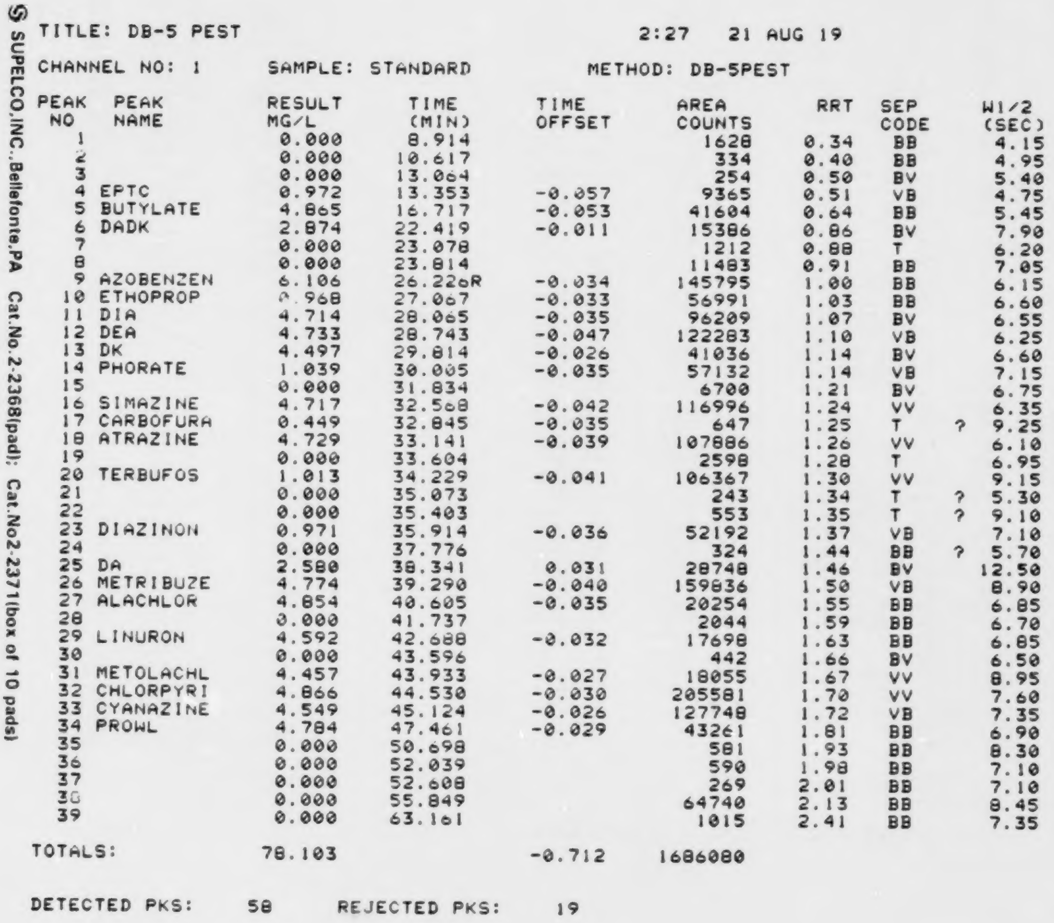


Figure 5.3. Typical chromatographs and data reports for a mixed pesticide standard on a DB-5 (Channel 1) and a DB-1 (Channel 2) column. Figure 5.3a. Chromatographs for Channels 1 and 2;

SUPELCO,INC.,Bellefonte,PA Cat.No.2-2368(pad); Cat.No2-2371(box of 10 pads)



```
TITLE: DB-5 PEST                                               2:27   21 AUG 19

CHANNEL NO: 1        SAMPLE: STANDARD            METHOD: DB-5PEST

PEAK  PEAK           RESULT      TIME        TIME          AREA       RRT   SEP          W1/2
 NO   NAME           MG/L        (MIN)       OFFSET        COUNTS           CODE         (SEC)
   1                 0.000       8.914                       1628     0.34   BB           4.15
   2                 0.000      10.617                        334     0.40   BB           4.95
   3                 0.000      13.064                        254     0.50   BV           5.40
   4 EPTC            0.972      13.353      -0.057           9365     0.51   VB           4.75
   5 BUTYLATE        4.865      16.717      -0.053          41604     0.64   BB           5.45
   6 DADK            2.874      22.419      -0.011          15386     0.86   BV           7.90
   7                 0.000      23.078                       1212     0.88   T            6.20
   8                 0.000      23.814                      11483     0.91   BB           7.05
   9 AZOBENZEN       6.106      26.226R     -0.034         145795     1.00   BB           6.15
  10 ETHOPROP        0.968      27.067      -0.033          56991     1.03   BB           6.60
  11 DIA             4.714      28.065      -0.035          96209     1.07   BV           6.55
  12 DEA             4.733      28.743      -0.047         122283     1.10   VB           6.25
  13 DK              4.497      29.814      -0.026          41036     1.14   BV           6.60
  14 PHORATE         1.039      30.005      -0.035          57132     1.14   VB           7.15
  15                 0.000      31.834                       6700     1.21   BV           6.75
  16 SIMAZINE        4.717      32.568      -0.042         116996     1.24   VV           6.35
  17 CARBOFURA       0.449      32.845      -0.035            647     1.25   T       ?    9.25
  18 ATRAZINE        4.729      33.141      -0.039         107886     1.26   VV           6.10
  19                 0.000      33.604                       2598     1.28   T            6.95
  20 TERBUFOS        1.013      34.229      -0.041         106367     1.30   VV           9.15
  21                 0.000      35.073                        243     1.34   T       ?    5.30
  22                 0.000      35.403                        553     1.35   T       ?    9.10
  23 DIAZINON        0.971      35.914      -0.036          52192     1.37   VB           7.10
  24                 0.000      37.776                        324     1.44   BB      ?    5.70
  25 DA              2.580      38.341       0.031          28748     1.46   BV          12.50
  26 METRIBUZE       4.774      39.290      -0.040         159836     1.50   VB           8.90
  27 ALACHLOR        4.854      40.605      -0.035          20254     1.55   BB           6.85
  28                 0.000      41.737                       2044     1.59   BB           6.70
  29 LINURON         4.592      42.688      -0.032          17698     1.63   BB           6.85
  30                 0.000      43.596                        442     1.66   BV           6.50
  31 METOLACHL       4.457      43.933      -0.027          18055     1.67   VV           8.95
  32 CHLORPYRI       4.866      44.530      -0.030         205581     1.70   VV           7.60
  33 CYANAZINE       4.549      45.124      -0.026         127748     1.72   VB           7.35
  34 PROWL           4.784      47.461      -0.029          43261     1.81   BB           6.90
  35                 0.000      50.698                        581     1.93   BB           8.30
  36                 0.000      52.039                        590     1.98   BB           7.10
  37                 0.000      52.608                        269     2.01   BB           7.10
  38                 0.000      55.849                      64740     2.13   BB           8.45
  39                 0.000      63.161                       1015     2.41   BB           7.35

TOTALS:             78.103                  -0.712        1686080

DETECTED PKS:     58      REJECTED PKS:     19
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Figure 5.3b. Data report for a DB-5 column (Channel 1);

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```
TITLE: DB1701-PEST                                     2:27   21 AUG 19

CHANNEL NO: 2       SAMPLE: STANDARD                METHOD: DWAXPEST

PEAK  PEAK          RESULT      TIME        TIME       AREA      RRT   SEP          W1/2
 NO   NAME          MG/L       (MIN)        OFFSET     COUNTS          CODE        (SEC)
   1                 0.000      7.265                     777   0.25   BB       4.55
   2                 0.000      7.902                     226   0.28   BB    ?  4.40
   3                 0.000      9.145                    4752   0.32   BB       6.20
   4                 0.000     10.843                    3099   0.38   BB       5.25
   5  EPTC           1.033     14.965       -0.045      18399   0.52   BB       5.45
   6                 0.000     15.816                     519   0.55   BB       6.70
   7                 0.000     16.813                     719   0.58   BB       8.95
   8  BUTYLATE       5.121     17.820       -0.050      83902   0.62   BB       5.80
   9                 0.000     28.112                     856   0.98   BB       7.40
  10  AZOBENZEN      6.385     28.780R      -0.030     218352   1.00   BB       6.20
  11  ETHOPROP       0.968     31.682       -0.038     147144   1.10   BV       7.50
  12                 0.000     32.218                     845   1.12   T     ?  7.50
  13  PHORATE        1.421     33.999       -0.031     165208   1.18   BV       7.85
  14  PROPOXUR       0.288     34.190       -0.040      20514   1.19   T     ?  8.95
  15                 0.000     34.670                    2238   1.21   T       10.30
  16                 0.000     36.718                    4297   1.28   BB      11.10
  17  TERBUFOS       1.031     37.611       -0.039     110965   1.31   BV       7.75
  18                 0.000     38.222                     174   1.33   T     ?
  19  FONOFOS        1.012     38.614       -0.036     570232   1.34   VV    ? 13.80
  20  DIA            4.815     38.906       -0.024      85275   1.35   T       12.15
  21  CARBOFURA      0.723     40.491       -0.049       3878   1.41   T       10.15
  22  ATRAZINE       4.968     40.712       -0.038     185547   1.41   VV       6.35
  23  SIMAZINE       5.045     40.952       -0.028     249983   1.42   VV       6.75
  24                 0.000     42.216                     404   1.47   T     ?  7.70
  25                 0.000     42.917                     969   1.49   BB       6.50
  26                 0.000     44.362                     374   1.54   BV       6.35
  27                 0.000     44.647                   12741   1.55   VB       7.30
  28  ALACHLOR       4.966     45.870       -0.030      37854   1.59   BB       7.00
  29  CYPRAZINE      4.950     46.611       -0.029     165051   1.62   BV       6.55
  30  METRIBUZE      4.834     47.162       -0.028      97976   1.64   VV       6.70
  31  CHLORPYRI      4.959     47.925       -0.025     544243   1.66   VV       7.90
  32  METOLACHL      4.929     49.029       -0.031      30474   1.70   T        9.60
  33  MALATHIO       0.697     49.825       -0.015       3912   1.73   T       15.35
  34                 0.000     50.145                     103   1.74   T     ?
  35  DA             3.125     51.254       -0.006      62357   1.78   BV       8.05
  36  PROWL          5.085     52.008       -0.042      81585   1.81   VV       7.05
  37                 0.000     52.863                    1259   1.84   T        7.30
  38                 0.000     55.788                    1900   1.94   BB       8.55
  39  CYANAZINE      4.791     57.608       -0.032     170082   2.00   BB       6.90
  40                 0.000     59.822                    1086   2.08   BB       7.65
  41                 0.000     64.504                     458   2.24   BB       9.75
  42                 0.000     67.047                    1983   2.33   BV       9.15
  43                 0.000     67.623                     725   2.35   VB    ? 12.30

TOTALS:             71.146                  -0.686    3093440

DETECTED PKS:      55     REJECTED PKS:      12
```

Figure 5.3c. Data report for a DB-1 column (Channel 2).

Table 5.5. Approximate detection limits and ranges of linear response in nanograms per liter, based on analysis of dilution series of mixed standards, and mean percent recoveries of spikes.

Pesticide	Detection Limit	Linear Range	Mean Percent Recovery 1983	1984	1985
Herbicides					
Alachlor (Lasso)	100	>500		104	64
Atrazine (Aatrex)	50	>500		86	69
Butylate (Sutan)	50	>200		73	70
Cyanazine (Bladex)	250	>500		98	79
EPTC (Eradicane, Eptam)	50	nd		76	66
Linuron (Lorox, Linurex)	1500	>5000		- -	80
Metolachlor (Dual)	250	>250		87	67
Metribuzin (Sencor, Lexone)	100	>2500		54	65
Pendimethalin (Prowl)	50	nd		80	71
Simazine (Princep)	250	>2500		88	74
Insecticides					
Carbofuran (Furadan)	200	>500		89	77
Fonofos (Dyfonate)	50	>150		60	57
Terbufos (Counter)	100	nd		76	54

SECTION 6

RESULTS AND DISCUSSION: SEDIMENTS AND NUTRIENTS

6.1. SEDIMENT AND NUTRIENT CONCENTRATIONS

The measurement of pollutant concentrations in streams and rivers is a fundamental component of many water quality studies. The resulting concentration data can be used to address a variety of water quality issues. For example, the concentration data can be:

1. compared directly with water quality standards to assess ambient water quality at the sampling site.
2. combined with flow data to calculate pollutant transport (both watershed export and watershed loading to downstream receiving waters).
3. analyzed to assess pollutant sources, transport pathways, and processing within the watershed and stream system. .

Since this sampling program focuses on storm runoff events, it provides detailed information on the effects of nonpoint pollution sources on both ambient water quality and pollutant transport. For many pollutants, such as sediment, nitrate, pesticides, and some forms of phosphorus, the highest pollutant concentrations occur during runoff events. Some water quality management agencies propose the establishment of high-flow water quality standards (Wlble 1980). If such standards are applied to agriculturally derived pollutants, they would have to take into account several of the characteristics of pollutant runoff described below.

6.1.1. Hydrograph, Sedigraph and Chemograph Patterns

One method of presenting chemical concentration data for streams and rivers and the relationships between chemical concentrations and stream discharge is to plot both discharge and concentrations as a function of time. Examples of such plots are shown in Figure 6.1. This figure contains an annual hydrograph, a sedigraph for suspended solids (SS) and chemographs for total phosphorus (TP), soluble reactive phosphorus (SRP), nitrate + nitrite-nitrogen (NO23-N) and conductivity (conductance) for the Sandusky River at Fremont during the 1985 water year. From the annual patterns it is evident that during periods of storm runoff events, concentrations of SS, TP and NO23-N all increase while the concentration of total dissolved solids, as reflected in the conductivity of the samples, decreases. Comparable plots for each station for the 1982-1985 water years are shown in Appendix I. In comparing the Appendix I graphs, note that the concentration and discharge scales are different on each graph. The computer program that draws the plots arbitrarily sets full scale at 110% of the highest concentration or discharge that occurred at that station in that year.

The changes in chemical and sediment concentrations during storm events in Lake Erie tributaries follow typical patterns (Figure 6.2) for both small watersheds (e.g., Lost Creek, 11.3 sq. km.) and the large river basins (e.g., the Maumee River, 16,395). During a runoff event, stream flow increases very rapidly on the rising limb of the hydrograph, reaches a

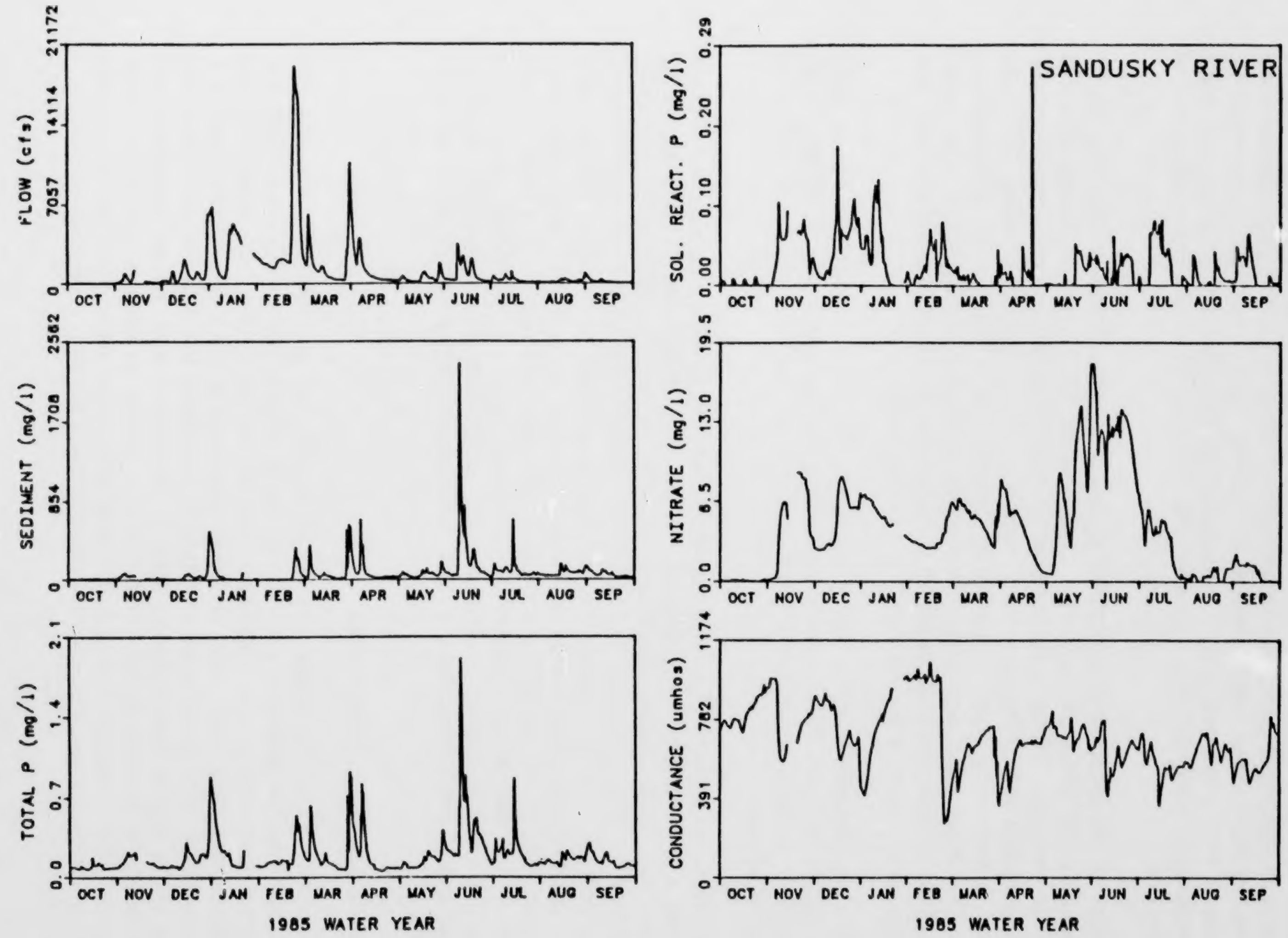

Figure 6.1. Annual hydrograph, sedigraph and chemograph of TP, SRP, NO23-N and conductivity at the Sandusky River transport station during the 1985 water year.

peak value and then decreases more slowly on the falling limb of the hydrograph. Sediment concentration peaks early in the runoff event and usually begins to decrease before the peak discharge occurs. Advanced peaks of sediment concentration relative to peak discharge are much more common than simultaneous or trailing peak sediment concentrations. Simultaneous or trailing sediment peaks are occasionally observed during "compound" storm events with multiple hydrograph peaks or when a localized storm occurs in a small portion of a large watershed.

Since most of the phosphorus transported during storms is attached to sediment, the TP concentrations closely follow the concentration pattern for SS. During the falling portion of the hydrograph, however, TP concentrations do not decline as rapidly as SS concentrations. This can be attributed both to the presence of soluble phosphorus forms, including SRP in the streams and to increasing ratios of particulate phosphorus to SS, as SS concentrations decrease. The latter effect is probably due to decreasing average particle sizes (e.g., increasing proportions of clays) accompanying decreasing SS concentrations (Johnson and Baker, 1982). The clay particles are typically enriched with phosphorus.

NO23-N concentrations increase during the falling limb of the hydrograph. In the study area, most of the NO23-N enters streams via tile drainage and interflow (Logan 1978). Water from these sources comprises a larger proportion of the total flow during the falling limb of the hydrograph.

The concentration patterns of soluble herbicides, such as atrazine, are distinct from both the sediments and the nitrates. As discussed further in Section 7.2.1, atrazine apparently moves off the fields with surface runoff water, but with different timing than for sediments. One hypothesis for this difference is that for SS, there is apparently a "pool" of highly erodible material on the soil surface. This material largely moves off fields with the early portions of the surface runoff water. Subequent surface water runoff has much lower sediment concentration. However, the surface runoff water continuously interacts with the upper zone of the soil surface, dissolving materials, such as pesticides, which have accumulated therein. The kinetics of dissolution may account for a relatively slow "leaching" of pesticides out of this surface layer of soil, and the resulting broad peaks of pesticide chemographs.

6.1.2. Concentration-Flow Relationships

Water quality data for rivers are often plotted as scattergrams showing the concentrations of various parameters in relationship to stream flow. In Figures 6.3 and 6.4, the data from Figure 6.1 (i.e., the Sandusky River at Fremont for the 1985 water year) are replotted as scattergrams, using linear scales in Figure 6.3 and log10 scales in Figure 6.4. Log transformations of this type of data are often used to spread the data out from the left and bottom axes of the graphs. These data illustrate the large amount of "scatter" associated with the concentrations of material derived from nonpoint sources in streams and rivers. Even with this scatter, it is evident that for SS, TP and NO23-N, concentrations tend to increase with increasing discharge, while conductivity tends to decrease with increasing discharge.

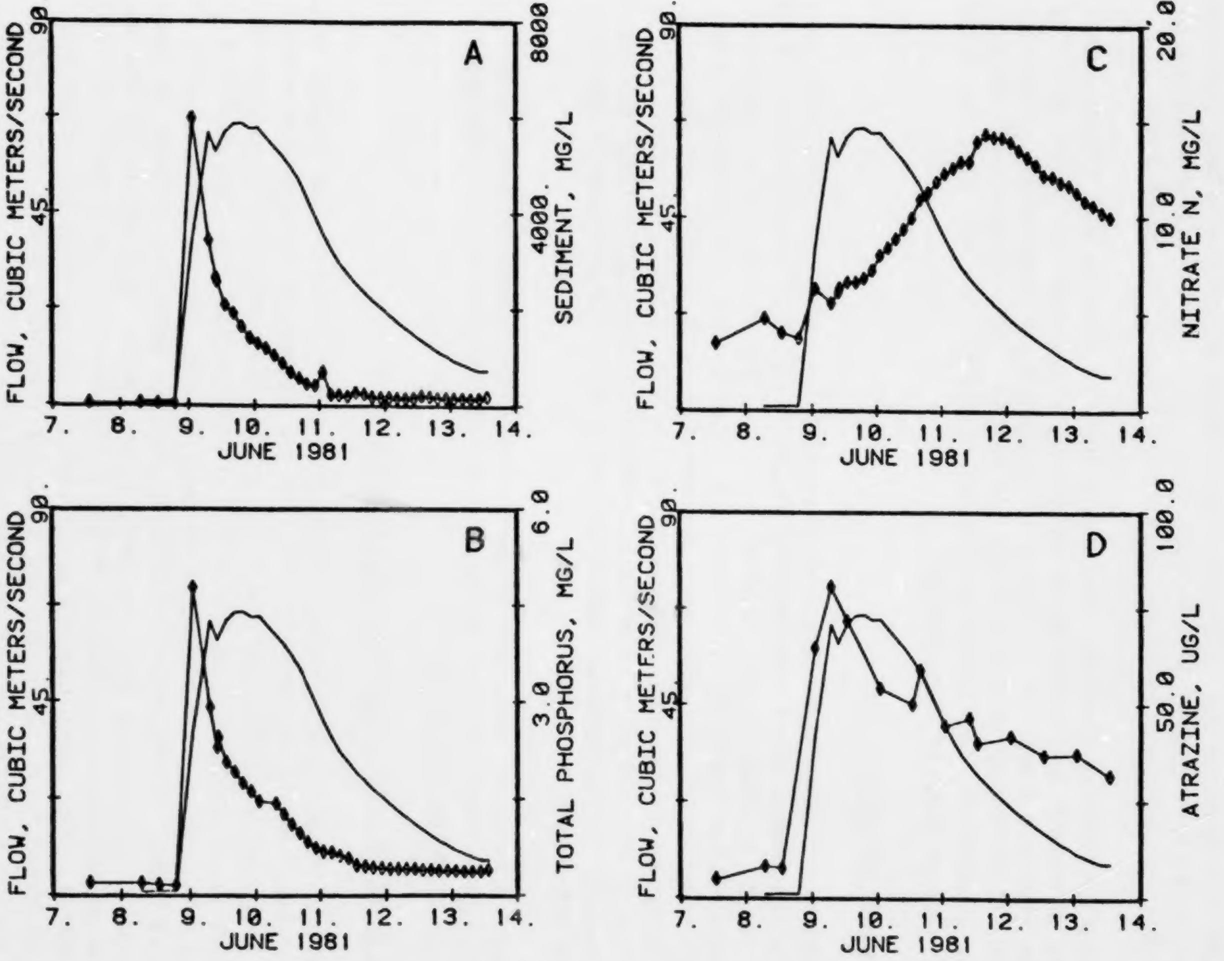

Figure 6.2. Typical pattern of concentration changes during a runoff event, as illustrated in June 1981 at the Honey Creek station near Melmore, Ohio. Solid line represents the hydrograph. Connected diamonds represent: A. SS; B. TP; C. NO23-N; D. atrazine.

Many factors contribute to the scatter in these plots. Storm discharge values less than the peak discharge occur twice during each storm, once on the rising limb of the hydrograph and once on the falling limb. The corresponding sediment and nutrient concentrations differ greatly on the rising and falling limbs of the hydrograph. Furthermore, discharge values which are near the peak discharge for small storms also occur near the beginning of the rising limb and ending of the falling limb of the hydrograph for large storms, again yielding large differences in concentrations for that discharge. Storms with the same peak discharge can have very different concentrations depending on the season, on the rainfall intensities, on the ground cover conditions and on antecedent soil moisture conditions (Baker 1984).

In order to characterize chemical water quality from the standpoint of either ambient water quality or loading, it is necessary to adequately characterize the "cloud" of points illustrated in Figures 6.3 and 6.4. It should be noted that, for a particular station, the characteristics of the "cloud" change from year to year in relation to weather conditions. Furthermore, documenting improvements in water quality requires detecting significant trends in the characteristics of these "clouds".

6.1.3. Frequency Histograms

The distribution of pollutant concentrations in streams can also be presented in the form of frequency histograms. Since the sampling frequency varies with stream flow, biases associated with the stratified sampling need to be removed from the data. Thus, rather than plot the number of samples falling within each concentration range, the percentage of time during which concentrations fall within each concentration range is plotted. In Figure 6.5, frequency histograms for the concentrations of SS, TP, and NO23-N, are shown for the Sandusky River at Fremont using all of the samples collected during the 1982-1985 water years. It is evident that the frequency with which various concentrations occur in streams is not normally distributed.

In Figure 6.6 frequency histograms for log transformed concentration data are shown. While the histogram for SS (Figure 6.6) appears "normal" following log transformation, the histograms for TP and NO23-N do not.

6.1.4. Time Weighted and Flux Weighted Mean Concentrations

If the concentrations of a chemical in a stream (or in a drinking water supply) were measured continuously during some time interval, the associated average concentration during that time interval provides one way to characterize the exposure of organisms living in that stream (or of people drinking that water) to that chemical. For most chemicals of interest, concentrations are not measured continuously. Instead, they are measured either at fixed intervals (daily, weekly, monthly, annually, etc.) or according to some stratified sampling program designed to more efficiently achieve some objective. In our studies, sampling frequencies are increased during periods of high flows in order to more accurately measure material loading. Since nonpoint source pollutant concentrations tend to be higher during runoff events, this same stratified sampling program provides more detailed information during the periods when concentrations tend to be highest.

The procedures used to estimate the average concentration differ slightly, depending on whether a fixed interval or a stratified sampling program was utilized. Fixed interval concentration measurements can be directly averaged since each sample characterizes the stream for the same length of time. The accuracy of the calculated average concentration depends on how well the selected frequency of sampling characterizes the actual occurrence of the chemical in the stream. For a stratified sampling program, individual samples do not characterize the stream for equal lengths of time. Thus, to estimate the average concentration, each sample has to be "weighted" according to the length of time it is used to represent the stream system. The resulting "time weighted mean concentration" (TWMC) provides an estimate of the average concentration in which biases introduced by the stratified sampling program (in this case, more frequent sampling during periods of high concentration) are removed. The TWMC is calculated using the following formula:

$$\text{TWMC} = \frac{\sum c_i t_i}{\sum t_i}$$

where

c_i is the chemical concentration of the i^{th} sample and

t_i is the duration of time that the i^{th} sample is used to characterize the stream concentration. It is equal to 1/2 the time interval between the samples immediately preceeding and following the i^{th} sample.

Often "average concentrations" in a stream are intended to characterize the export of material from the stream system rather than the average exposures within the stream. In this case, the desired average concentration would be the concentration observed if all of the stream discharge were collected over the time period of interest and the resulting concentration was measured. In practice, this average concentration is estimated by weighting the individual samples by their associated flows. The resulting average concentration is referred to as a flow (or flux) weighted mean concentration. Where stratified sampling is used, it is necessary to also weight individual samples by their associated time period. We refer to the resulting average concentration as the "flux weighted mean concentration" (FWMC). It is calculated as follows:

$$\text{FWMC} = \frac{\sum c_i t_i q_i}{\sum t_i q_i} = \frac{\text{Total Load}}{\text{Total Discharge}}$$

where

q_i is the instantaneous discharge at the time of the i^{th} sample.

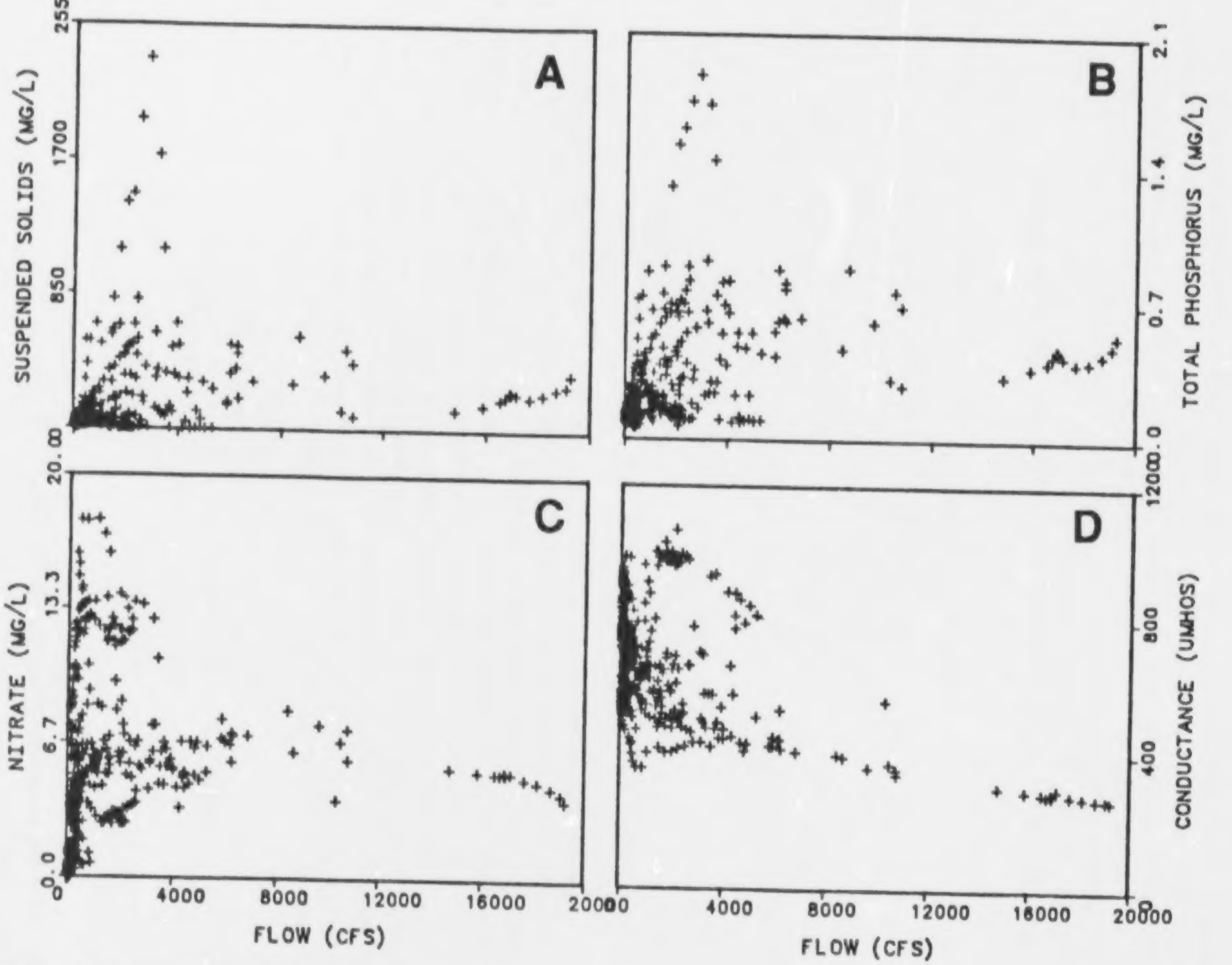

Figure 6.3. Scattergrams of SS, nutrient and conductivity concentrations in relationship to stream discharge for the 1985 water year at the Sandusky River station. A. SS; B. TP; C. NO23-N; D. Conductivity.

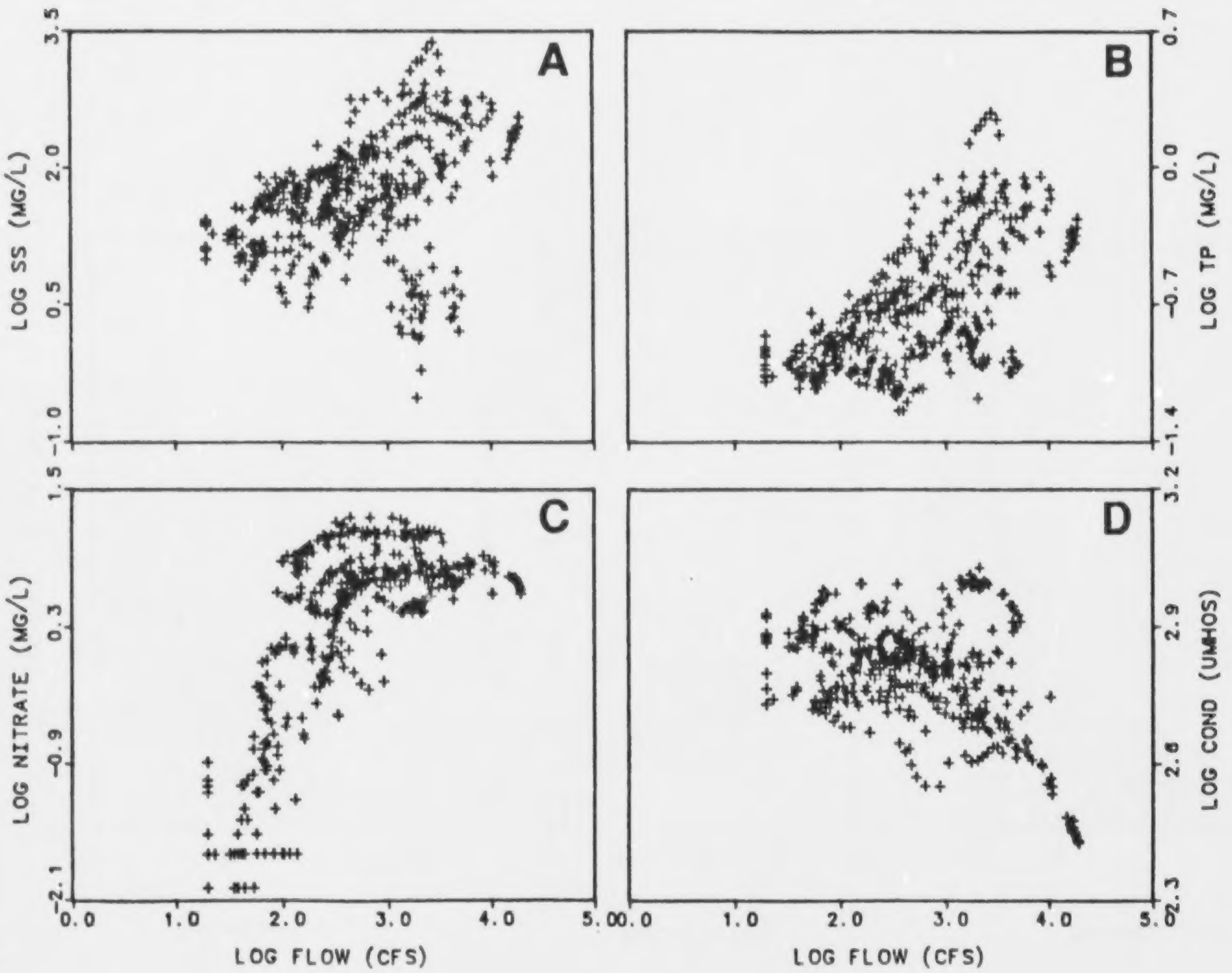

Figure 6.4. Scattergrams based on log transformed data of SS, nutrient and conductivity concentrations in relationship to stream discharge. Same data as Figure 6.3. A. SS; B. TP; C. NO23-N; D. Conductivity.

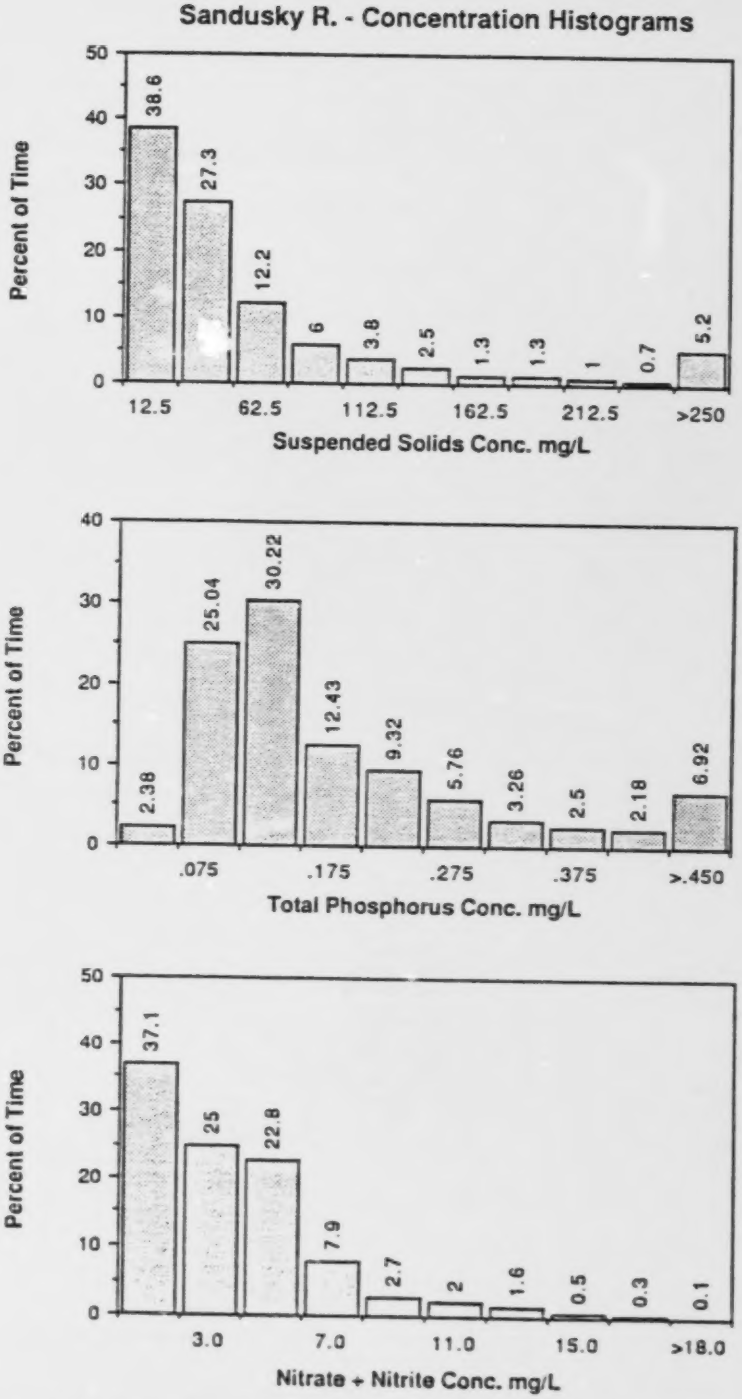

Figure 6.5. Histograms illustrating the percentage of time concentrations fall within given ranges. Data from the Sandusky River, 1982-1985 water years. A. SS; B. TP; C. NO23-N.

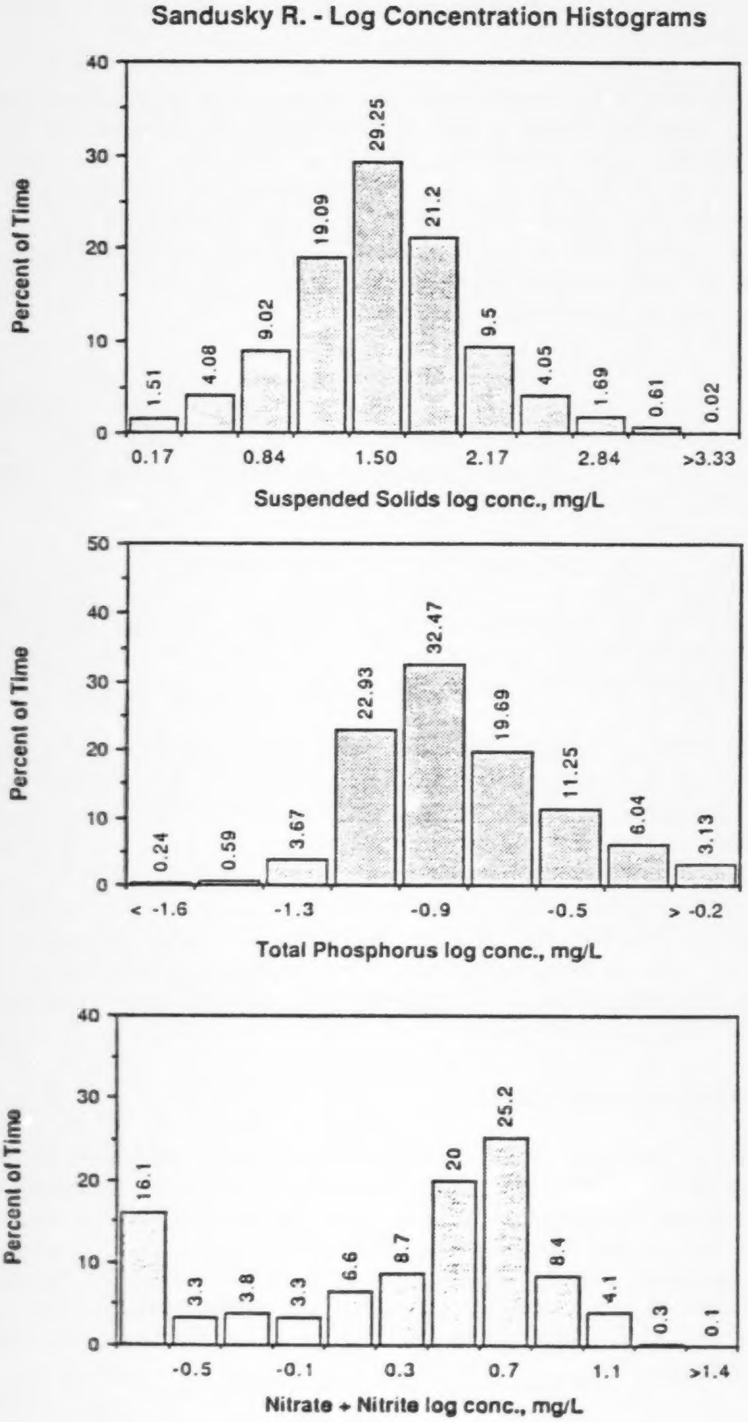

Figure 6.6. Histograms illustrating the percentage of time concentrations (log transformed data) fall within given ranges. A. SS; B. TP; C. NO23-N.

It should be noted that the FWMC is equivalent to the total load divided by the total discharge for the period of interest.

The TWMC's and the FWMC's for nutrients and sediments at each of the transport stations for the 1982-1985 water years are shown in Table 6.1. It is evident from Table 6.1 that there is considerable difference between the TWMC's and the FWMC's. For sediments and TP the annual FWMC is often 2 or more times the TWMC. Ratios of FWMC to TWMC (i.e., FWMC/TWMC) greater than 1 indicate that, for the overall data set, the concentrations tend to increase with increasing discharge. Increasing concentrations with increasing discharge are characteristic of materials derived from the surface runoff component (and the tile drainage component) of nonpoint source pollution.

Where there are significant point sources of a pollutant, the concentrations of that pollutant tend to decrease with increasing stream flow and the accompanying increase in dilution of the point source input. This results in FWMC to TWMC ratios <1.0. For the Cuyahoga River the TWMC's of SRP are greater than the FWMC's of SRP suggesting that point sources are a significant part of the SRP input into that river.

The FWMC/TWMC ratios also reflect the relative contributions of surface runoff water to groundwater for major rivers. For chloride and conductivity, TWMC's are greater than FWMC's (Table 6.2). Runoff water from land surfaces generally has much lower chloride levels and conductivity than does water derived from interflow or groundwater. The latter sources contribute most of the water present in streams during low flow conditions.

The differences between TWMC's and FWMC's are large and important. Unfortunately, in many studies, the distinction between TWMC's and FWMC's are ignored. For example, in the modelling studies conducted by Resources for the Future (RFF) (Gianessi et al 1986) as a basis for establishing national pollution control policies for governmental agencies, sediment and nutrient concentrations are estimated from loading and discharge estimates (i.e., they are FWMC's) but the same concentration values are interpreted as reflecting average ambient water quality concentrations (i.e., as TWMC's). While the RFF model attempts to include the effects of in-stream material processing, the failure to distinguish between TWMC's and FWMC's should raise significant questions regarding the adequacy of the model as a basis for even "broad brush" policy development.

6.1.5. Concentration Exceedency Curves

With respect to ambient water quality, information regarding peak pollutant concentrations may be more important than TWMC's. Also it may be especially important to know the duration of time a pollutant exceeds some critical value. While chemographs such as those in Figure 6.1 and Appendix I do indicate peak concentrations, concentration exceedency curves and tables are more useful in assessing the duration of various concentration ranges. In Figure 6.7, the same data contained in Figure 6.1 are plotted in the form of concentration exceedency curves. Again, the individual samples are time weighted to remove bias associated with stratified sampling.

One use of concentration exceedency curves is to illustrate the duration of time particular concentrations (such as water quality standard) are exceeded. For example, in

Table 6.1. Comparisons of time weighted mean concentrations (TWMC) and flux weighted mean concentrations (FWMC) for sediments and nutrients at Lake Erie Basin transport stations.

Station	Year	SS, mg/L		TP, mg/L		SRP, mg/L*		NO23-N, mg/L		TKN, mg/L	
		TWMC	FWMC	TWMC	FWMC	TWMC	FWMC	TWMC	FWMC	TWMC	FWMC
Maumee	1982	99.5	180	0.280	0.396	0.075	0.081	3.49	3.99	1.33	1.62
	1983	85.6	199	0.261	0.438	0.058	0.060	3.68	5.52	1.35	1.89
	1984	78.5	183	0.262	0.452	0.059	0.066	4.11	6.03	1.37	1.86
	1985	---	205	---	0.434	---	---	4.42	5.52	1.46	1.73
Sandusky	1982	96.7	283	0.221	0.460	0.049	0.065	3.02	3.59	1.13	1.84
	1983	48.6	164	0.144	0.362	0.035	0.055	2.99	5.57	0.87	1.52
	1984	72.6	144	0.233	0.399	0.048	0.084	3.54	3.74	1.13	1.60
	1985	72.4	178	0.190	0.351	---	---	4.30	5.74	1.03	1.45
Cuyahoga	1982	141.6	256	0.433	0.486	0.156	0.103	2.52	1.83	1.33	1.46
	1983	78.4	178	0.392	0.419	0.167	0.111	2.65	1.89	1.13	1.21
	1984	71.1	158	0.396	0.407	0.171	0.102	2.41	1.74	1.36	1.41
	1985	85.4	269	0.391	0.527	---	---	2.59	1.99	1.28	1.60
Raisin	1982	40.7	49	0.183	0.149	0.051	0.036	1.94	1.54	0.93	0.77
	1983	44.2	91	0.176	0.256	0.050	0.045	2.83	4.07	0.95	1.26
	1984	37.6	77	0.172	0.229	0.043	0.039	2.61	4.22	0.98	1.27
	1985	33.1	86	0.166	0.248	---	---	2.81	4.23	0.95	1.30
Honey Cr.	1982	82.2	252	0.211	0.441	0.056	0.059	3.83	3.77	1.15	1.87
	1983	45.4	133	0.174	0.355	0.058	0.056	4.10	5.72	0.95	1.67
	1984	48.0	127	0.212	0.375	0.066	0.075	4.49	4.20	1.05	1.54
	1985	37.6	125	0.169	0.348	---	---	5.22	6.35	0.99	1.64
Upper Honey Cr.	1982	25.8	---	0.100	---	0.028	---	2.52	---	0.72	---
	1983	41.1	175	0.114	0.337	0.028	0.058	3.12	5.64	0.75	1.81
	1984	48.6	212	0.157	0.447	0.043	0.085	2.60	3.96	0.79	1.76
	1985	29.4	190	0.092	0.388	---	---	3.04	5.77	0.59	1.51
Rock Cr.	1983	44.6	271	0.132	0.436	0.026	0.036	2.65	6.07	0.75	2.15
	1984	44.3	249	0.147	0.466	0.032	0.045	2.13	2.61	0.80	1.91
	1985	39.9	183	0.123	0.341	---	---	2.37	3.86	0.73	1.53

* No SRP data were obtained for the 1985 water year.

Table 6.2. Comparison of TWMC's and FWMC's for chloride and conductivity.

Station	Year	Chloride mg/L		Conductivity µmhos/cm	
		TWMC	FWMC	TWMC	FWMC
Maumee R.	1982	35.0	24.8	573.3	456.1
	1983	40.5	27.4	611.6	523.2
	1984	41.5	24.8	604.1	464.7
	1985	44.9	28.4	630.0	496.0
Sandusky R.	1982	36.1	21.7	640.9	426.2
	1983	42.2	30.1	736.6	588.6
	1984	29.3	20.3	555.0	417.3
	1985	40.4	33.6	685.7	600.1
Cuyahoga R.	1982	103.3	94.5	752.8	655.6
	1983	94.0	84.5	760.8	674.4
	1984	107.6	96.0	793.8	684.8
	1985	117.5	92.0	816.2	709.7
Raisin R.	1982	37.5	21.8	638.6	432.7
	1983	37.7	30.9	668.5	588.3
	1984	43.1	31.8	697.0	573.9
	1985	44.7	31.3	707.0	542.5
Honey Cr.	1982	24.9	17.1	557.2	341.8
	1983	28.0	21.6	607.2	447.7
	1984	23.2	15.0	533.5	331.5
	1985	30.2	20.8	616.2	388.9
Upper Honey Cr.	1982	28.8	24.0	657.6	452.7
	1983	29.0	26.4	658.7	509.3
	1984	23.9	16.0	581.1	353.0
	1985	31.6	20.6	691.9	390.1
Rock Cr.	1983	32.2	19.5	743.4	462.4
	1984	27.4	14.0	659.7	312.6
	1985	36.7	23.9	769.6	452.8

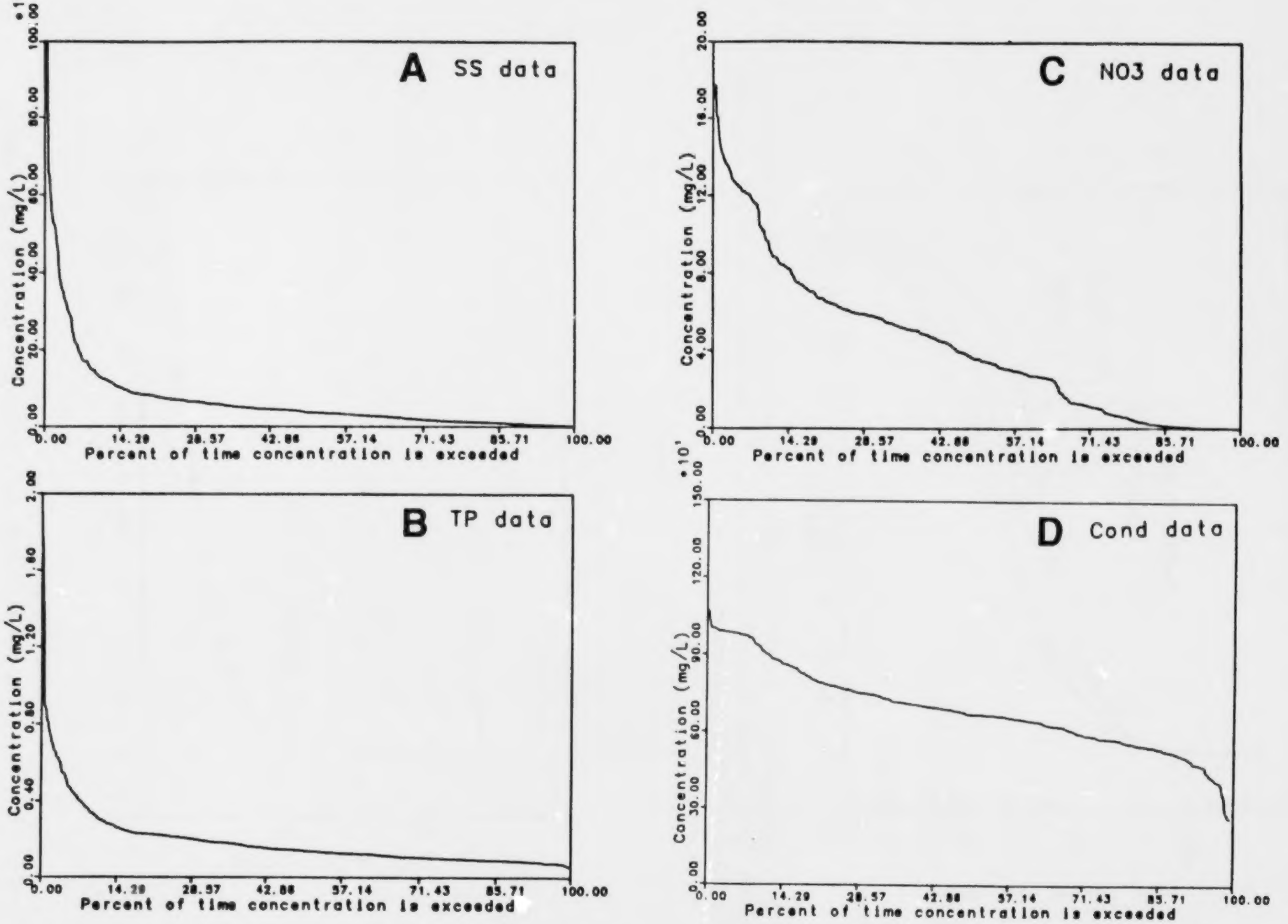

Figure 6.7. Concentration exceedency curves for SS(A), TP(B), NO23-N(C), and Conductivity(D) at the Sandusky River station during the 1985 water year.

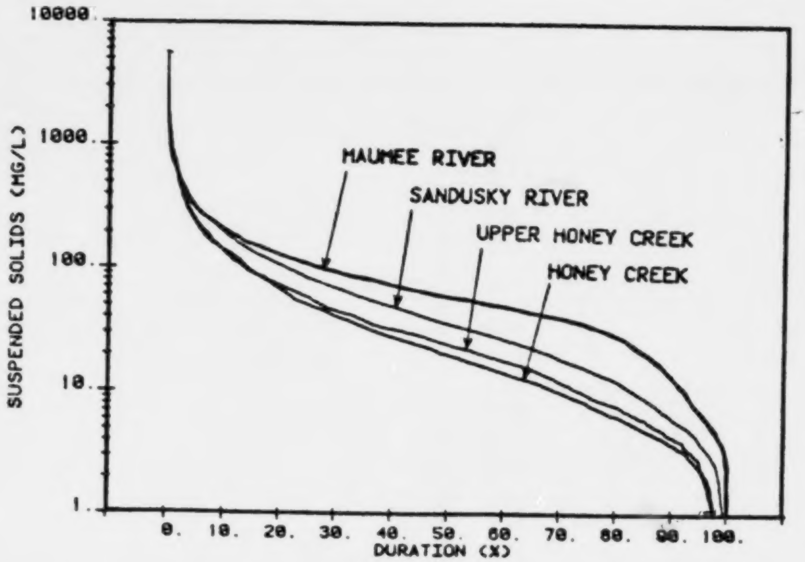

Figure 6.8. Concentration exceedency curves for suspended solids at the Maumee, Sandusky River, Upper Honey Creek and Honey Creek-Melmore stations. Data for the period of record at each station.

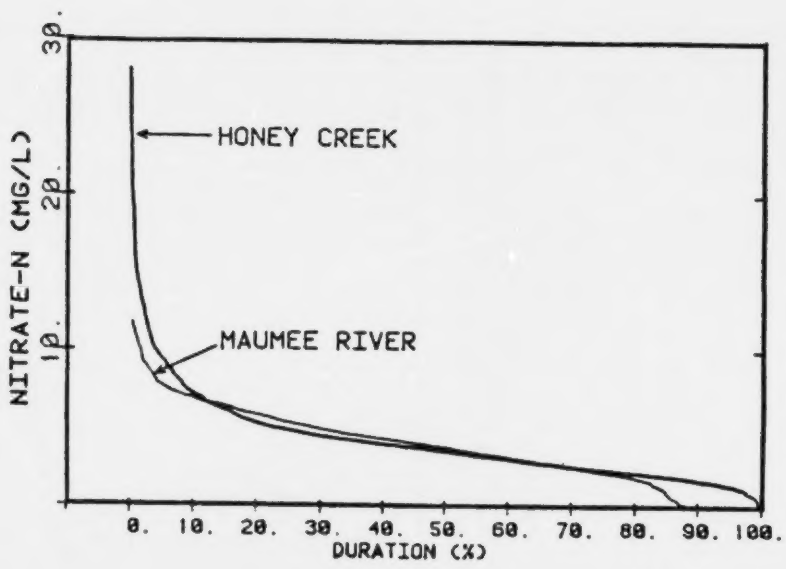

Figure 6.9. Concentration exceedency curves for NO23-N at the Honey Creek-Melmore and Maumee River stations. Data for the period of record at each station.

1985 the NO23-N standard of 10 mg/L was exceeded in the Sandusky River for about 11% of the time. Concentration exceedency graphs can also be used to compare the concentration patterns for different rivers. In Figure 6.8 concentration exceedency curves for the suspended solids concentrations (log scale) are shown for four of the river transport stations. It is clearly evident in Figure 6.8 that as the watershed size decreases, (Maumee>Sandusky>Honey Creek), the suspended solids concentrations are significantly lower for much of the time. The curves in Figure 6.8 do not reflect the fact that the peak sediment concentrations are higher for small watersheds than for large watersheds.

In Figure 6.9, NO23-N concentration exceedency curves are shown for the Maumee River and for Honey Creek. Honey Creek, the smaller watershed, has higher peak concentrations, but slightly lower ambient concentrations for much of the rest of the time.

Concentration exceedency data can also be presented in the form of exceedency tables. In such tables the values listed can show either concentrations exceeded for fixed percentages of time or the percentages of time particular concentrations are exceeded. In Tables 6.3-6.5, the concentrations of SS, TP and NO23-N that are exceeded fixed percentages of time are shown for seven of the transport stations for the 1982-1985 water years. The stations are listed in the sequence of decreasing watershed size. The TWMC and the FWMC for the combined 1982-1985 period are also shown for each parameter and period.

The data in Tables 6.3-6.5 provide an interesting example of the effects of watershed size on pollutant concentration patterns. The FWMC's of SS and TP are rather similar for all of the agricultural watersheds except for the River Raisin, which has lower concentrations. The TWMC's decrease as watershed size decreases. The concentrations exceeded 50% of the time correspond to the median concentrations. Note that the median values are lower than the TWMC's. Furthermore, these medians decrease even more than the TWMC's as watershed size decreases. The concentration patterns become skewed more and more to the left as watershed size decreases.

6.1.6. Seasonal Variations in Flux Weighted Mean Concentrations

The long term records (7-11 years) for the Maumee, Sandusky and Honey Creek watersheds, allow analyses of the seasonal aspects of pollutant concentrations in river systems. The FWMC's for SS, TP, SRP and NO23-N during the fall (Oct-Dec), winter (Jan-March), spring (April-June), and summer (July-Sept) periods are shown in Table 6.6. For SS, the highest concentrations occur in the spring period. The differences between the spring and the fall/winter concentrations are much larger for Honey Creek than for the Maumee River. Again, these differences are probably associated with watershed size. As watershed size decreases the peak sediment concentrations more closely coincide with the peak periods of soil erosion by high intensity spring storms which occur when crop cover is minimal. As watershed size increases, sediment transport is more closely associated with the movement of large storm runoff events through the river systems that wash out sediment previously deposited in the channel system. Many of the large runoff events occur in the winter.

While watershed size seems to have a significant effect on seasonal concentration patterns of SS and sediment-associated pollutants such as TP, watershed size has much less of an

Table 6.3. Concentrations of suspended solids (mg/L) exceeded fixed percentages of time for Lake Erie river transport during the 1982-1985 water years.

% of time listed conc. were equaled or exceeded	Sampling station and associated drainage area (Km^2)						
	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	- - - - - - - - - - - - - - - - - suspended solids, mg/L -						
0.2	1045	1542	532	2716	1196	892	945
0.5	798	1146	414	1289	811	680	592
1.0	634	744	305	954	538	481	385
2.0	462	504	203	665	367	370	258
5.0	286	253	118	329	197	173	125
10.0	184	146	70	176	110	79	71
25.0	85	68	39	67	45	31	34
50.0	53	33	26	30	22	18	16
TWMC	87.0	72.2	38.7	91.9	53.0	42.7	38.0
FWMC	197.0	181.9	82.1	209.3	159.8	240.8	176.4
Total Monitored time (hrs.)	33,349	31,145	26,527	31,705	33,998	23,419	25,591

Table 6.4. Concentrations of total phosphorus (mg/L) exceeded fixed percentages of time for Lake Erie river transport during the 1982-1985 water years.

% of time listed conc. were equaled or exceeded	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	Sampling station and associated drainage area (Km^2)						
	- - - - - - - - - - - - - - total phosphorus concentrations, mg/L - - - - - - - - - - - - - -						
0.2	1.194	1.712	0.905	2.571	1.557	1.324	1.578
0.5	1.090	1.382	0.798	1.625	1.176	0.949	1.014
1.0	0.971	0.912	0.596	1.260	0.873	0.780	0.819
2.0	0.812	0.725	0.457	1.086	0.654	0.622	0.598
5.0	0.577	0.529	0.321	0.722	0.485	0.434	0.382
10.0	0.449	0.376	0.255	0.577	0.376	0.271	0.252
25.0	0.282	0.226	0.198	0.452	0.218	0.140	0.116
50.0	0.201	0.134	0.158	0.348	0.142	0.090	0.070
TWMC	0.257	0.196	0.173	0.402	0.191	0.134	0.118
FWMC	0.432	0.388	0.241	0.452	0.381	0.433	0.395
Total Monitored time (hrs.)	33,349	31,145	26,527	31,705	33,998	23,419	25,591

Table 6.5. Concentrations of nitrate plus nitrite-nitrogen (mg/L) exceeded fixed percentages of time for Lake Erie river transport during the 1982-1985 water years.

% of time listed conc. were equaled or exceeded	Sampling station and associated drainage area (Km^2)						
	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	- - - - - - - - - - - - - - - - nitrate plus nitrite-nitrogen, mg/L - - - - - - - - - - - - - -						
0.2	17.3	17.7	12.0	7.2	25.4	16.0	21.0
0.5	15.9	14.9	10.3	6.3	20.5	14.9	19.4
1.0	14.0	13.6	8.4	6.1	17.8	12.7	16.2
2.0	11.0	12.2	7.2	5.5	14.4	9.4	9.7
5.0	8.4	9.5	6.2	4.8	9.5	6.5	7.4
10.0	7.1	7.0	5.4	4.3	7.0	5.1	5.8
25.0	6.0	5.0	3.7	3.2	5.2	3.1	4.1
50.0	4.1	3.2	2.1	2.3	3.8	1.8	2.4
TWMC	3.93	3.48	2.61	2.54	4.42	2.35	2.87
FWMC	5.29	4.22	3.66	1.85	4.57	3.28	4.55
Total Monitored time (hrs.)	33,349	31,145	26,527	31,705	33,998	23,419	25,591

Table 6.6. Seasonal and annual flux weighted mean concentrations of sediments and nutrients for the period of record at long-term transport stations.

Watershed	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sep	Overall
	Flux weighted mean concentrations (mg/L)				
			Suspended Solids		
Honey Creek	72	133	381	221	203
Sandusky River	125	206	409	226	249
Maumee River	179	205	272	140	216
			Total Phosphorus		
Honey Creek	0.294	0.346	0.598	0.407	0.417
Sandusky River	0.332	0.444	0.603	0.402	0.464
Maumee River	0.445	0.473	0.531	0.360	0.479
			Soluble Reactive Phosphorus		
Honey Creek	0.088	0.074	0.060	0.098	0.074
Sandusky River	0.083	0.093	0.062	0.085	0.082
Maumee River	0.092	0.095	0.071	0.092	0.087
			Nitrate + Nitrite-Nitrogen		
Honey Creek	4.84	3.85	6.16	4.67	4.82
Sandusky River	4.87	3.73	6.19	3.35	4.57
Maumee River	5.25	3.76	5.87	4.39	4.82

interaction with the seasonal concentrations of soluble constituents. For all of the watersheds, NO23-N concentrations are highest in the spring but the ratio of spring concentrations to the concentrations in other seasons is similar. Whether the high spring concentrations of NO23-N are associated with the spring application of nitrogen fertilizers or the warming of the soil and subsequent increased nitrification by soil bacteria is uncertain.

For all three watersheds, SRP concentrations were lowest in the spring. The seasonal variation in SRP may reflect differences in the amounts of SRP processing within the stream system, due to biological activity and/or sediment adsorption.

6.1.7. Effects of Watershed Size on Peak Pollutant Concentrations

Plots of concentration exceedency curves allow convenient comparisons of pollutant concentrations over much of the concentration and duration range. However, comparison of peak concentrations on concentration exceedency graphs is more difficult (see Figure 6.8). In Table 6.7 the peak concentration of SS and NO23-N for individual storm events are shown for four watersheds, ranging in size from 11.3 km^2 (Lost Creek) to 16,400 km^2 (Maumee

River). It is evident that the peak sediment concentrations in Lost Creek are much higher than the peak concentrations in the Maumee River. Peak concentrations for the other watersheds are intermediate in size. In comparing the peak sediment concentrations in Lost Creek with those observed in runoff from individual fields, the Lost Creek values are low. In the Four Mile Creek Watershed study in Iowa (Johnson and Baker 1982), peak sediment concentrations in storm runoff from a 5 ha and a 6 ha plot were an order of magnitude higher than those observed in Lost Creek.

It is likely that both sediment deposition and water routing contribute to the decreasing peak sediment concentrations with increasing watershed size. Comparison of the sedigraphs with the hydrographs (Figures 6.1 and 6.2) indicates that the distribution of high sediment concentrations within the hydrograph is largely confined to the front portion of the storm. As storm waters converge from various tributaries into a larger stream, they will be in different phases of their own hydrographs, thereby providing considerable water with low sediment concentration to mix with and dilute the water with high sediment concentrations.

In the case of nitrates, the peak concentrations are also higher in smaller watersheds than in larger watersheds. However, for nitrates, the ratios of peak concentrations for small to large watersheds are not nearly so large as similar ratios for sediments. This may be due to the fact that nitrates are distributed more broadly within the hydrograph than are sediments (Figures 6.1 and 6.2). Consequently, water routing through the channel system is accompanied by less dilution of nitrates.

6.1.8. Nitrate Contamination of Surface Waters and Drinking Waters

In northwestern Ohio, as elsewhere in the Midwest, several municipalities withdraw water for public water supplies directly from rivers. Since conventional water treatment procedures do not remove nitrates, the nitrate concentrations present in the rivers are also present in the finished water supplies. The nitrate concentrations in Lake Erie tributaries frequently exceed the drinking water standard of 10 mg/L nitrate-nitrogen, usually during the May-July period. In the case of the Sandusky River, which supplies drinking water for both Fremont and Tiffin, Ohio, the nitrate standard has been exceeded every year since the onset of our monitoring program in 1974. In 1985, the standard was exceeded continuously for 30 days.

For the period of record in the Sandusky River, nitrates exceeded the standard 4.1% of the time, but since these occurrences were always in the months of May, June or July, the standard was exceeded 16% of the time during these months. For the Sandusky, nitrates were in the range of 7-10 mg/L for about 12% of the time. If conservation tillage increases infiltration and, consequently, the proportion of stream water derived from tile effluents, it is likely that the percentage of time nitrates exceed the drinking water standard will increase.

6.1.9. Concentration Patterns for the New York Rivers

As was mentioned in Section 5.2, the sampling program for the New York tributaries is less dense than that for the Ohio rivers, and probably characterizes the important high-flow periods less adequately, for reasons discussed in that section. The average number of samples taken yearly on these rivers is about 50, as compared with 300 to 500 on the Ohio

Table 6.7. Peak suspended sediment and nitrate + nitrite-N concentrations observed during individual storm runoff events of the 1982, 1983 and 1984 water years in northwest Ohio rivers.

	Suspended Solids		Nitrate + Nitrite-N	
Watershed	Date	mg/L	Date	mg/L
Lost Creek	820330	13,744	830607	23.6
	830610	6,500	820523	22.6
11.3 km^2	820527	4,992	830629	19.0
	830615	4,376	840915	19.0
	840422	4,148	820528	16.2
	830710	3,935	830702	15.5
	820710	3,825		
	820715	3,690		
	840414	3,625		
	820719	3,316		
	820703	3,078		
Honey Creek	820528	5,238	820618	28.1
	820629	4,507	830703	20.1
386 km^2	820703	2,161	840708	19.3
	820331	1,681	840713	18.1
	820523	1,600	820529	15.8
	820312	1,241	820525	14.8
	840422	1,196		
Sandusky River	820528	2,037	820619	15.7
	840423	1,566	830629	12.9
3,240 km^2	820401	1,437	820529	12.2
	820317	1,417	840710	12.1
	830703	1,171	820706	11.5
	840626	1,146		
Maumee River	820105	1,694	820528	12.3
	840427	1,067	830702	11.4
16,395 km^2	820529	1,045	831113	10.8
			840525	10.6
			820607	10.3

tributaries. While these data are less dense than we would wish, they still provide some indication of the concentrations which are characteristic of the rivers. Table 6.8 compares the TWMC's and the FWMC's for the New York tributaries. Flow data can be found in Table 5.1.

A comparison of data for the New York rivers with data (Tables 6.1 and 6.2) for the Sandusky and Maumee Rivers, which are comparable in size, suggests that:

1. the Genesee has comparable SS and Cond, high Cl, lower TP and SRP, and much lower NO23-N and TKN. The difference in comparability of Cond and Cl suggests that the major ion composition of these two waters is significantly different.

2. The Oswego has higher Cond, much higher Cl, and much lower SS, TP, SRP, NO23-N, and TKN concentrations.

3. The Black has consistently much lower concentrations of all parameters.

Comparison of the TWMC's with the FWMC's suggests that the New York tributaries as a group respond less to runoff events with changes in concentration than do the Ohio tributaries to Lake Erie. Of the three, the Genesee seems most event-responsive, the Black is intermediate, showing responses only in SS and TP, and the Oswego is the most stable, with only SS concentrations suggesting event responsiveness. These relationships between the three are consistent with their relative sizes and with the relatively low level of agriculture in the Black River watershed.

6.2. SEDIMENT AND NUTRIENT LOADING IN LAKE ERIE TRIBUTARIES

6.2.1. Loading Calculations

Sampling programs of the type underway in these studies allow a direct calculation of nutrient and sediment loading. These calculations are similar to the mid-interval technique that the U.S. Geological Survey uses to calculate sediment loads at daily sediment stations (Porterfield 1972). The automatic samplers are set to collect "on the hour," i.e., at 0100, 0700, 1300, and 1900 hours. Where more frequent samples are collected during storm events, the times of sample collection are listed by a printer interfaced to the sampler. The USGS provides hourly gauge height data in the form of provisional reports for each station. The gauge height at the time of sample collection is added to our data file for each sample. A rating table, relating gauge height to discharge, is also provided by the USGS and stored on our computer for each station. The rating table is used, together with the gauge height information, to determine the instantaneous stream discharge at the time of sample collection. On occasions when the stage recording equipment fails, the USGS estimates mean daily flows based on relationships to adjacent stream gauges. These estimated mean daily flows appear in the U.S.G.S. Water Resources Data for each state and water year are used in our calculations when gauge height data are unavailable.

Table 6.8. Time weighted mean concentrations (TWMC) and flux weighted mean concentrations (FWMC) for the New York tributaries to Lake Ontario. In the calculations, each sample was allowed to represent up to 200 hours of time. See text for a discussion of the way we determine how much time each sample represents.

Parameter	Year	Genesee		Oswego		Black	
		TWMC	FWMC	TWMC	FWMC	TWMC	FWMC
SS, mg/L	1982	125.1	230.7	9.84	9.52	6.79	15.22
	1983	49.3	62.8	13.75	20.06	10.60	16.97
	1984	196.4	254.5	15.44	17.42	11.83	17.00
	1985	68.6	162.6	12.28	12.06	6.62	8.86
	Overall	123.3	215.1	13.00	15.70	8.75	14.05
TP, mg/L	1982	0.141	0.227	0.074	0.072	0.032	0.040
	1983	0.064	0.073	0.077	0.074	0.036	0.050
	1984	0.193	0.248	0.071	0.071	0.040	0.051
	1985	0.094	0.175	0.077	0.074	0.018	0.021
	Overall	0.136	0.214	0.075	0.072	0.032	0.040
SRP, mg/L	1982	0.016	0.016	0.027	0.026	0.004	0.003
	1983	0.007	0.007	0.017	0.011	0.004	0.005
	1984	0.005	0.006	0.004	0.003	0.001	0.003
	1985	<0.000>	<0.000>	0.004	0.005	<0.000>	<0.000>
	Overall	0.008	0.008	0.014	0.013	0.002	0.002
NO23-N, mg/L	1982	1.08	1.16	0.768	0.787	0.482	0.528
	1983	1.07	1.05	0.636	0.744	0.389	0.438
	1984	1.38	1.35	0.752	0.794	0.422	0.484
	1985	1.10	1.19	0.463	0.487	0.476	0.509
	Overall	1.14	1.21	0.649	0.754	0.421	0.464
TKN, mg/L	1982	0.610	0.763	0.774	0.781	0.468	0.477
	1983	0.402	0.425	0.727	0.751	0.420	0.509
	1984	0.707	0.801	0.626	0.635	0.340	0.380
	1985	0.642	0.822	0.841	0.827	0.310	0.350
	Overall	0.620	0.758	0.740	0.731	0.392	0.424
Cl, mg/L	1982	57.5	42.7	141.1	128.4	2.41	1.95
	1983	70.0	64.4	197.7	136.6	2.88	2.81
	1984	48.0	41.0	148.6	125.7	2.44	2.45
	1985	86.1	65.4	357.6	335.1	2.67	2.53
	Overall	63.1	47.5	207.4	141.6	2.55	2.33
Conductivity, µmhos/cm	1982	544.4	447.1	864	801	94.6	88.8
	1983	610.8	571.8	1141	877	108.9	109.1
	1984	483.9	434.7	894	798	94.9	93.9
	1985	718.4	594.6	1480	1423	76.9	73.3
	Overall	579.1	474.9	1091	859	97.2	93.0

The instantaneous flux of each nutrient or sediment is calculated as the product of the sample concentration times the instantaneous discharge. This instantaneous flux is assumed to characterize the river transport for a specific time interval associated with that sample. This time interval (or time multiplier) is equivalent to one-half the time interval between that sample and the preceeding sample plus one-half the time interval between that sample and the following sample. The time interval that any sample can be used to characterize the loading rate can be limited to a particular value. For our nutrient and sediment loading calculations we usually limit the maximum time interval to 24 hours. Multiplying the instantaneous flux for each sample by the time interval for each sample gives a total load for the time period associated with that sample. Summing the total loads for all the individual samples yields the total load for the time period covered by the sampling program. The formula for the load calculation is:

$$\text{Total Load} = \sum c_i t_i q_i$$

where

c_i = concentration of the i^{th} sample

q_i = instantaneous discharge at the time of collection of the i^{th} sample

t_i = is the time interval associated with the i^{th} sample
It corresponds to 1/2 the time interval between the samples immediately preceeding and following the i^{th} sample.

Since the loading calculations described above are based on provisional hourly stage data supplied by the USGS rather than on final USGS discharge data, the loading values obtained by the above techniques are adjusted to the final USGS discharge data as described below. These adjustments are done for the reporting of monthly and annual loads (See Table 6.10 and Appendix I). The adjustments also allow corrections for time intervals not characterized by instantaneous discharge data or the chemical sampling program, due to breakdown in the pumping system, automatic samplers, or analytical systems.

Table 6.9 consists of a computer printout from the program used for adjusting monthly and annual loads to final USGS discharge data. In this case the printout is for total phosphorus loading from the Maumee River during the 1984 water year. The program is run separately for each parameter, each water year and each station. The program calculates an observed total load for each month using the sampling program for that month, and the instantaneous discharges as described above. For each month the number of samples (N), the flux weighted mean concentration (FWMC), sum of the time multipliers, (cumulative time) the total observed discharge (observed flow), and the total load (observed flux) is listed. Water year totals for the number of samples analyzed, the cumulative time, the observed flow and the observed flux are also shown. An observed flux weighted mean for the water year, obtained by dividing the total observed load by the total observed flow, is also listed.

Final USGS monthly discharges, as presented in the Water Resources Data series for each state and water year, are stored in data files accessed by the program. These USGS flows for each month, along with the ratio of the USGS flow to the observed flow for that month are also listed in the program printouts. The program then multiplies the observed flux by the flow ratio yielding a calculated (or adjusted) flux for each month. For months where the flow ratio is >1.5 and the USGS monthly flow is 10% or more of the USGS annual discharge, the suitability of the observed FWMC for that month is subjectively assessed. The assessment involves comparison with the FWMC for that particular month over the entire period of record. Depending on the extent of missing flow data (and associated samples), the observed FWMC is either replaced by or averaged with the FWMC for that month from the period of record. The revised FWMC is manually multiplied by the USGS flow for that month to produce a revised calculated monthly flux. The calculated monthly fluxes, including any manual revisions, are added to provide a calculated flux for the water year. This calculated value represents the annual load for that station as presented in this report (e.g. Table 6.11 and Figures 6.10-6.12). The calculated flux for the water year is divided by the total USGS water year discharge to determine an adjusted FWMC which is also shown on the computer generated tables. The FWMC's reported in Table 6.1 are the adjusted FWMC's generated by this computer program, as modified by any manual corrections.

After the above program has been run for each parameter for a given station and water year, the monthly and annual loads for major nutrients and sediments are summarized as illustrated in Table 6.10. Note that the last column of the loading worksheet (Table 6.9) showing monthly calculated fluxes of total phosphorus is the same as the column for TP in Table 6.10. The summary includes the USGS discharge for each month, the ratio of the USGS discharge to the discharge calculated from the sampling program, the number of samples analyzed each month, and the calculated monthly loads of SS, TP, SRP, NO23-N, TKN, and chloride (Cl). Water year totals for each of the above are also shown. A table similar to Table 6.10 is included in Appendix I for each station and each water year from 1982-1985.

6.2.2. Annual Loads and Unit Area Loads for Lake Erie Tributaries

The annual loads for the major parameters for each station and water year are shown in Table 6.11. The Maumee River, which has the largest watershed, has the largest sediment and nutrient loads. The Sandusky and Cuyahoga rivers also have substantial loads of sediments and nutrients. Annual variability in loads is evident for all parameters and stations.

In Table 6.12, unit area yields of sediments and nutrients are shown for each station and water year. These unit area yields are all calculated by dividing the annual yields (Table 6.11) by the total watershed area upstream from each sampling station. The Cuyahoga River has the highest unit area yields of sediments, total phosphorus, soluble reactive phosphorus, and chlorides. In fact, the unit area chloride export from the Cuyahoga River is four to five times higher than that of any other of the Lake Erie tributaries currently monitored. Whether these high chloride export rates are associated with industrial or municipal point sources, with geological features or with some other source is uncertain. The high unit area export of soluble reactive phosphorus is likely to be derived from municipal point sources. As noted earlier, the concentrations of soluble reactive phosphorus at this station are higher under low flow conditions than under high flows, suggesting point source origins. The unit area nitrate export for the Cuyahoga River is much lower than for the watersheds dominated by row crop agriculture.

```
                                WATER QUALITY LAB
                                HEIDELBERG COLLEGE
03-Dec-86

Flux Comparison for MAUMEE
Parameter:   TP
Water year:  1984

Month     N      FWMC      Cum. Time   Obs. Flow      USGS Flow      Flow Ratio   Obs. Flux     Calc. Flux
                 mg/L        hours       m**3           m**3                      Metric Tons   Metric Tons

Oct.      36     .212885   751         .797967E+08    .844068E+08    1.05777      16.9875       17.9689

Nov.      53     .556125   711         .6784E+09      .616688E+09    .909033      377.275       342.956

Dec.      37     .44282    753         .111943E+10    .101232E+10    .904324      495.704       448.277

Jan.      35     .196659   738         .748888E+08    .760283E+08    1.01522      14.7275       14.9516

Feb.      34     .318432   660         .960514E+09    .789769E+09    .822236      305.858       251.487

Mar.      40     .376246   696         .109575E+10    .113695E+10    1.0376       412.272       427.773

Apr.      66     .648432   720         .141911E+10    .13089E+10     .922341      920.194       848.733

May       37     .429087   738         .596606E+09    .541692E+09    .907957      255.996       232.433

June      34     .263132   720         .161358E+09    .165067E+09    1.02299      42.4584       43.4344

July      36     .159178   744         .381856E+08    .552019E+08    1.44562      6.07829       8.78691

Aug.      40     .207369   738         .43935E+08     .589678E+08    1.34216      9.11075       12.2281

Sept.     34     .199739   708         .190265E+08    .325475E+08    1.71064      3.80033       6.501
        ------   --------  -------     ----------     -----------                 ---------     ----------
          482    .454981   8677        .628699E+10    .587854E+10                 2860.46       2655.53


  Adjusted FWMC:    .451733
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Table 6.9. Sample printout from program used to adjust monthly and annual loads to the final USGS discharge data as published in the U.S.G.S. Water Resources Data for each state and water year.

Table 6.10. Monthly loads and discharge for the Maumee River for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	84.41	1.058	36	3786	18.0	5.42	273	101.8	5401.7
Nov	616.69	0.909	53	137804	343.0	48.26	4837	1386.9	17371.3
Dec	1012.32	0.904	37	128897	448.3	66.96	6118	1806.6	20496.0
Jan	76.03	1.015	35	286	15.0	10.93	335	104.0	4350.3
Feb	789.77	0.822	34	60073	251.5	86.68	3374	1504.4	26552.7
Mar	1136.95	1.038	40	183798	427.8	64.15	7336	1935.6	22843.8
Apr	1308.90	0.939	66	432218	848.7	53.89	7874	2850.1	24007.1
May	541.69	0.908	37	103840	232.4	38.88	4160	863.7	13064.8
Jun	165.07	1.023	34	17607	43.4	9.90	982	189.6	4412.6
Jul	55.20	1.446	36	2741	8.8	1.14	76	59.1	2820.9
Aug	59.00	1.342	40	3328	12.2	2.06	78	76.1	3168.3
Sep	32.55	1.711	34	1930	6.5	0.95	7	42.4	2021.0
Totals	5878.54		482	1076310	2655.5	389.22	35449	10920.1	146510.0

Table 6.11. Sediment and nutrient loads (metric tons) at the Lake Erie Basin transport stations for the 1982-1985 water years.

Station	Year	SS	TP	SRP	NO23-N	TKN	SiO2	Cl
Maumee	1982	1,280,000	2,820	576	28,400	11,500	40,100	168,000
	1983	947,000	2,080	286	26,200	8,900	32,300	131,000
	1984	1,080,000	2,660	389	35,450	10,920	38,300	146,500
	1985	897,000	1,900		24,100	7,560	40,200	128,000
Sandusky	1982	393,000	639	90.0	4,900	2,560	7,580	30,500
	1983	106,800	235	35.7	3,620	988	4,110	19,800
	1984	280,000	773	162	7,250	3,100	11,200	37,900
	1985	137,000	270		4,420	1,100	7,060	25,500
Cuyahoga	1982	235,500	447	94.8	1,680	1,340	5,950	86,800
	1983	164,150	386	102	1,740	1,120	5,940	76,300
	1984	163,100	419	105	1,790	1,460	6,950	99,100
	1985	247,600	486		1,830	1,470	8,800	97,600
Raisin	1982	45,000	138	32.9	1,430	708	3,060	13,900
	1983	79,500	224	39.6	3,560	1,100	5,890	27,100
	1984	57,600	173	29.4	3,180	960	5,050	24,300
	1985	69,900	202		3,450	1,060	7,920	26,500
Honey Cr.	1982	39,720	69.6	9.30	595	295	856	2,770
	1983	11,800	31.5	5.01	508	148	626	1,920
	1984	21,420	63.0	12.7	707	259	1,074	2,570
	1985	11,440	31.8		580	150	806	1,950
Upper Honey Cr.	1983	1,940	4.17	.645	62.4	20.0	88.5	276
	1984	4,470	9.42	1.79	83.4	37.0	147	340
	1985	2,300	4.68		69.7	18.2	116	271
Rock Cr.	1984	10,700	20.1	1.95	113	82.3	236	621
	1985	3,620	6.76		76.6	30.3	169	486

Table 6.12. Unit area yields of sediments and nutrients at the Lake Erie tributary transport stations for the 1982-1985 water years.

Station	Year	SS kg/ha	TP kg/ha	SRP kg/ha	NO23-N kg/ha	TKN kg/ha	SiO2 kg/ha	Cl kg/ha
Maumee	1982	781	1.72	.351	17.3	7.01	24.5	102.5
	1983	577	1.27	.114	16.0	5.48	19.7	79.8
	1984	656	1.62	.237	21.6	6.66	23.3	89.4
	1985	547	1.16		14.7	4.61	24.5	77.9
Sandusky	1982	1213	1.97	.278	15.4	7.90	23.4	94.1
	1983	330	.727	.110	11.2	3.05	12.7	61.1
	1984	864	2.39	.501	22.4	9.57	34.7	117
	1985	422	.833		13.6	3.43	21.8	78.7
Cuyahoga	1982	1286	2.44	.518	9.18	7.32	32.5	474
	1983	896	2.11	.559	9.49	6.09	32.4	417
	1984	891	2.29	.575	9.77	7.95	38.0	541
	1985	1352	2.65		9.99	8.04	48.1	533
Raisin	1982	167	.511	.122	5.30	2.62	11.3	51.5
	1983	295	.829	.147	13.2	4.08	21.8	100
	1984	214	.640	.109	11.8	3.56	18.7	89.9
	1985	259	.750		12.8	3.94	29.3	98.0
Honey Cr.	1982	1029	1.80	.241	15.4	7.64	22.2	71.8
	1983	307	.817	.130	13.2	3.84	16.2	49.8
	1984	555	1.63	.328	18.3	6.70	27.8	66.5
	1985	296	.824		15.0	3.88	20.9	50.4
Upper Honey Cr.	1983	441	.948	.147	14.2	4.55	20.1	62.7
	1984	1016	2.14	.407	19.0	8.41	33.3	77.3
	1985	522	1.06		15.8	4.14	26.3	61.5
Rock Cr.	1984	1218	2.28	.221	12.8	9.35	26.8	70.6
	1985	411	.768		8.71	3.44	19.2	55.2

The River Raisin has the lowest sediment, total phosphorus and nitrate export rates of the watersheds dominated by agricultural land uses. It is noteworthy that the average gross erosion rate for the River Raisin (Table 5.2) is higher than that of any of the Ohio tributaries to Lake Erie. The low sediment and nutrient yields from the River Raisin illustrate a lack of correlation between high gross erosion rates and high unit area yields of sediments and nutrients (Baker et al. 1985b).

6.2.3. Annual Variability in Nutrient and Sediment Export

Agricultural nonpoint source pollution is characterized by a large amount of annual variability. This annual variability is illustrated in Figures 6.10, 6.11 and 6.12 which depict the seasonal and annual rainfall, discharge and loads of SS, TP, SRP and NO23-N for the period of chemical transport studies at the Maumee, Sandusky and Honey Creek stations. Each bar in the graphs of Figures 6.10 - 6.12 is composed of four segments representing the four seasons. The fall period (Oct.-Dec.) is at the base of each bar, followed by the winter period (Jan.-Mar.), and the spring period (April-June), with the summer period (July-Sept.) at the top of each bar. The rainfall data for the Maumee are based on the average from 17 NOAA weather stations located in northwest Ohio and the Maumee River Basin. For the Sandusky River, the rainfall data are based on the average of the 11 NOAA weather stations in north central Ohio, four of which are in the Sandusky Basin and five adjacent to the basin.

In Table 6.13 the means and coefficients of variation for annual rainfalls, discharges and loads of SS, TP, SRP, and NO23-N are listed, based on data collected through the 1985 water year. Using data from Table 6.13 together with the bar graphs of Figures 6.10-6.12 the following generalizations regarding variability in annual export can be made.

1. Total annual rainfall is the least variable of the factors monitored.

2. Total stream discharge is much more variable than is total rainfall. Rainfall intensities and timing, relative to soil moisture content, are apparently more important in influencing seasonal and annual discharge than is the total amount of rainfall.

3. As watershed size decreases, the annual variability in sediment and total phosphorus load increases, and for smaller watersheds is much greater than the annual variability in discharge.

4. The variability in the export of soluble nutrients such as SRP and NO23-N is similar to the variability in discharge.

6.2.4. Seasonal Distribution of Material Export

In Table 6.14 the percentage of material export occurring during each season for the entire period of record is shown for the three watersheds with the longest records. With

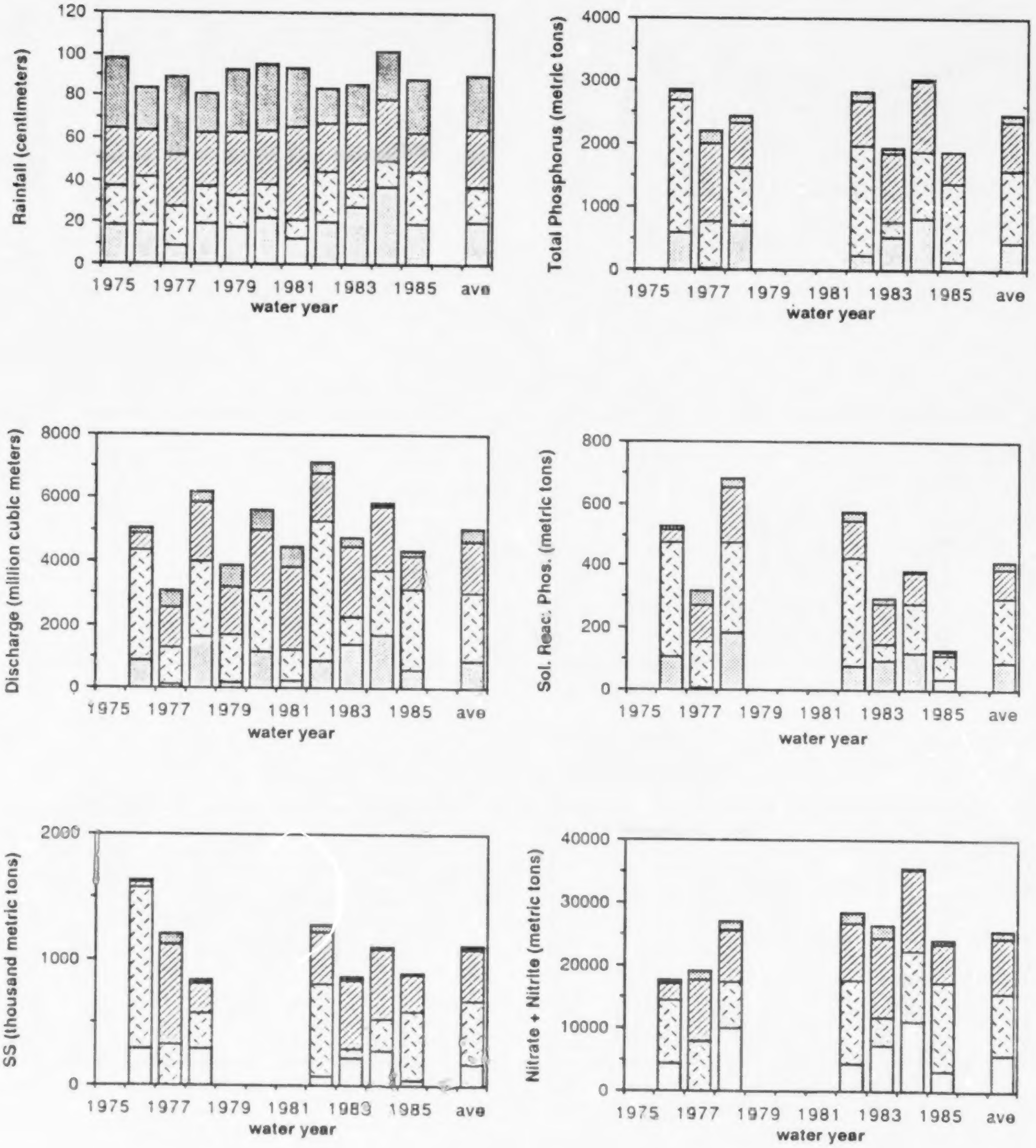

Figure 6.10. Annual variability and seasonal distribution of rainfall, discharge and loading of SS, TP, SRP and NO23-N at the Maumee River transport station.

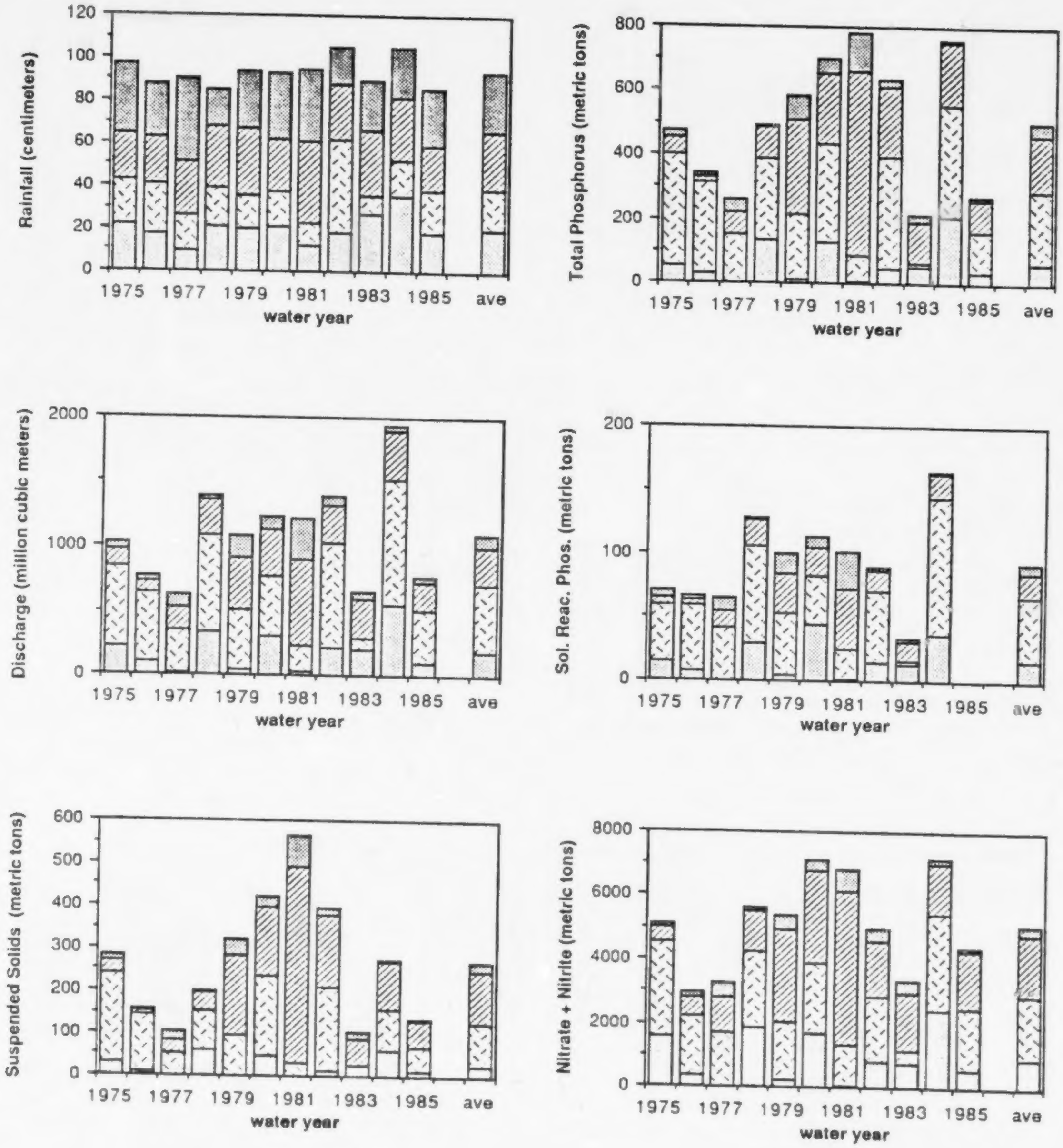

Figure 6.11. Annual variability and seasonal distribution of rainfall, discharge and loading of SS, TP, SRP and NO23-N at the Sandusky River transport station.

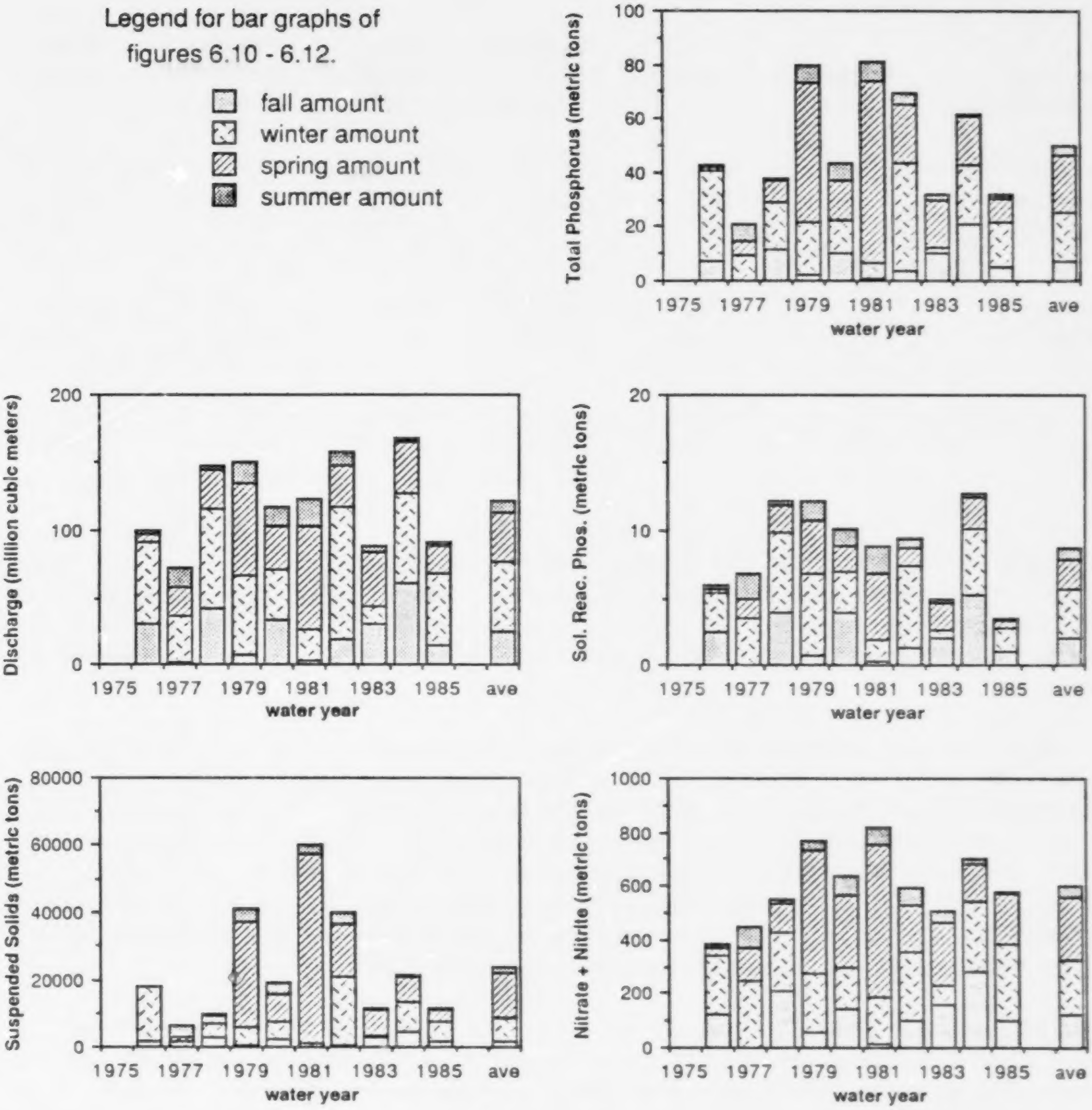

Figure 6.12. Annual variability and seasonal distribution of discharge and loading of SS, TP, SRP and NO23-N at the Honey Creek transport station. Rainfall patterns at Honey Creek would be similar to those at the Sandusky River transport station.

Table 6.13. Means and coefficients of variation for annual rainfall and discharge and for annual export of sediments and nutrients from three northwestern Ohio watersheds of varying sizes.

Watershed (Years of data)	Rainfall cm	Discharge $10^6 m^3$	Suspended Solids 10^3 metric tons	Total Phosphorus metric tons	Soluble Reactive Phosphorus metric tons	Nitrate + Nitrite-Nitrogen metric tons
Honey Creek (10 years)		122 ±27.%	24.0 ±73.%	50.2 ±43.%	8.67 ±37.%	600 ±23.%
Sandusky R. (11 years)	93.7 ±7.%	1100 ±36.%	269 ±55.%	503 ±41.%	93.3 ±40.%	5110 ±30.%
Maumee R. (7 years)	90.2 ±7.%	5030 ±24.%	1120 ±25.%	2460 ±19.%	417 ±46.%	25500 ±24.%

respect to rainfall, the spring and summer have the largest amounts, with about 50% more rainfall during these seasons than during the fall and winter period. Discharges are, however, much greater during the winter than for spring and fall, with the least amount in the summer. Watershed size seems to have little effect on the seasonal distribution of discharge.

For suspended sediments in Honey Creek, the spring accounted for 57% of the total export with the winter accounting for only 27%. In contrast, in winter the Maumee River transported 42% of the sediment, while the spring accounted for 37%. The Sandusky River was intermediate in terms of the seasonality of sediment export. As noted by McGuinness et al. (1971) in smaller watersheds sediment export is more closely tied to the timing of soil erosion events on the landscape while for larger rivers, sediment export coincides more closely with the timing of stream discharge. The seasonal patterns of total phosphorus export for the three watersheds are similar to those for suspended solids.

The seasonal distribution of soluble phosphorus export is similar to the seasonal distribution of discharge, except that winter is even more important for soluble phosphorus export. The sources of the soluble phosphorus exported during winter are uncertain. It is possible that the freezing of vegetation releases soluble phosphorus that is subsequently exported. As noted in Section 6.1.7 it is also possible that there is less processing of SRP during winter, resulting in greater SRP concentrations and export.

For NO23-N the winter and spring periods are large and equally important, followed in importance by the fall season. There is very little nitrate export during the summer period. The lower spring discharges are accompanied by higher nitrate concentrations (Section 6.1.7), resulting in loads similar to those exported in the winter time with its higher discharges and lower nitrate concentrations.

Table 6.14. Seasonal distribution of rainfall, discharge and nutrient sediment export from three northwest Ohio watersheds of varying sizes.

	Percent of mean annual load			
	Oct-Dec	Jan-Mar	April-June	July-Sept
		Rainfall		
Honey Creek [see Sandusky R.]				
Sandusky R.	21.5	20.4	28.7	29.3
Maumee R.	22.3	18.8	30.4	28.7
		Discharge		
Honey Creek	19.8	42.8	29.8	7.4
Sandusky R.	17.4	46.8	27.4	8.5
Maumee R.	17.2	42.3	33.0	7.6
		Suspended Sediment		
Honey Creek	7.5	28.3	55.8	8.2
Sandusky R.	9.0	38.7	45.0	7.7
Maumee R.	15.5	44.3	36.8	3.1
		Total Phosphorus		
Honey Creek	14.3	35.7	42.6	7.3
Sandusky R.	12.6	44.5	35.4	7.3
Maumee R.	17.7	46.3	32.2	3.6
		Soluble Reactive Phosphorus		
Honey Creek	24.1	41.8	24.2	10.0
Sandusky R.	17.9	52.5	20.7	8.9
Maumee R.	21.6	49.2	23.7	5.4
		Nitrate + Nitrite-Nitrogen		
Honey Creek	20.0	34.7	38.3	7.0
Sandusky R.	18.3	38.4	37.4	6.0
Maumee R.	22.8	38.0	34.8	4.4

Watershed size seems to have little effect on the seasonal aspects of the export of soluble constituents including both SRP and NO23-N.

6.2.5. Role of High Flux Periods in Total Material Export

Since the transport of materials derived from nonpoint sources occurs primarily during storm runoff periods, it is not surprising that large proportions of material export occur during small proportions of time. In Tables 6.15-6.17, the roles of periods of high fluxes in the export of SS, TP and NO23-N are presented for watersheds of various sizes. For SS, the 0.5% of the time with the highest fluxes accounted for 17% of the total export for the Maumee and 48% of the total export for Upper Honey Creek. In general, as watershed size decreases, small percentages of time with the highest flux rates account for increasing proportions of the SS and TP export. It should be noted that the 0.5% of the time (or any other of the percentages listed) does not represent a continuous time interval during a single storm event, but rather the periods of peak flux rates during several different storm events. The program that produces the values presented in Table 6.15-6.17 ranks the instantaneous flux rates, thereby picking out short time intervals with high flux rates from all of the runoff events of that station.

The data as presented in Tables 6.15-6.17 underscore the importance of obtaining samples during the relatively small proportion of time with high flux rates even though these periods may constitute short periods of many individual storms. As watershed sizes become smaller, the time windows which must be carefully sampled to produce accurate loading data also become smaller. Monte Carlo analyses of data sets for the Maumee, Sandusky and Honey Creek stations indicated that more samples are required in small watersheds than in large watersheds to achieve a given level of precision and accuracy in load estimation (Richards and Holloway 1985a,b).

NO23-N, with 0.5% of the time accounting for 5% of the NO23-N export from the Maumee and 16% from Upper Honey Creek. The export of particulate phosphorus probably corresponds more closely to SS export while the export of SRP, which is also included in the TP measurements, probably is more like the export of nitrates. It should be noted that the effects of watershed size on the durations of material export are important for both particulate and soluble constituents.

6.2.6. Gross Erosion Rates, Unit Area Sediment and Nutrient Yields and Sediment Delivery Ratios for Long Term Transport Stations

In Table 6.18 the average unit area yields of SS, TP, SRP, NO23-N, and TKN are listed for each of the long term transport stations. The average yields of total phosphorus and total nitrogen (NO23-N + TKN) for croplands in the United States, as used to estimate lake loadings (Rast and Lee 1983), are also shown in Table 6.18. The monitored yields for Lake Erie tributaries are much higher than the average yields from agricultural land. In the case of total nitrogen, the unit area yields for northwestern Ohio are equivalent to approximately 50% of the nitrogen fertilizer added to those watersheds each year. Thus the nitrogen losses via surface water (and associated tile systems) represent significant losses to farmers.

Table 6.15. Percentages of suspended solid loads that were exported during fluxes which were exceeded for the indicated percentages of time (e.g. for the Maumee River fluxes exceeded 1% of the time accounted for 27.1% of the total suspended solids export during the period encompassing the 1982-1985 water years).

Percent of time fluxes were exceeded	Sampling station and associated drainage area (Km^2)						
	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	% of total load exported						
0.5	17.3	24.3	17.8	28.3	32.9	42.7	48.2
1.0	27.1	36.4	26.9	38.1	45.7	59.5	63.5
2.0	41.3	50.9	41.3	51.0	60.6	76.6	77.9
5.0	64.3	73.1	64.2	69.4	78.8	93.2	92.0
10.0	81.6	87.7	79.6	81.5	89.9	97.6	96.6
20.0	93.9	95.4	91.2	90.9	97.0	99.0	98.8
50.0	98.9	99.3	97.7	98.3	99.7	99.8	99.7

Table 6.16. Percentages of total phosphorus loads that were exported during fluxes which were exceeded for the indicated percentages of time (e.g. for the Maumee River fluxes exceeded 1% of the time accounted for 17.2% of the total phosphorus export during the period encompassing the 1982-1985 water years).

Percent of time fluxes were exceeded	Sampling station and associated drainage area (Km^2)						
	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	% of total load exported						
0.5	9.8	14.8	14.8	13.2	18.1	30.9	32.8
1.0	17.2	22.8	23.9	18.0	27.4	47.2	46.7
2.0	28.7	35.2	33.4	26.0	40.4	64.0	62.2
5.0	48.9	58.3	51.5	39.4	63.0	86.4	82.7
10.0	67.5	77.3	67.9	51.3	80.8	93.9	93.0
20.0	85.6	90.2	81.3	64.8	92.8	97.2	97.4
50.0	97.6	98.5	92.9	85.1	99.1	99.3	99.5

Table 6.17. Percentages of nitrate plus nitrite-nitrogen loads that were exported during fluxes which were exceeded for the indicated percentages of time (e.g. for the Maumee River fluxes exceeded 1% of the time accounted for 8.6% of the total nitrate plus nitrite nitrogen export during the period encompassing the 1982-1985 water years).

Percent of time fluxes were exceeded	Sampling station and associated drainage area (Km^2)						
	Maumee 16,395	Sandusky 3,240	Raisin 2,699	Cuyahoga 1,831	Honey Cr. 386	Rock Cr. 88.0	Upper Honey Cr. 44.0
	- - - - - - - - - - - - - - - % of total load exported -						
0.5	5.0	6.9	5.3	3.0	9.1	17.9	16.3
1.0	8.7	12.3	9.5	5.2	15.1	28.8	26.2
2.0	15.3	20.4	17.3	8.7	24.3	44.9	39.6
5.0	31.9	37.8	34.1	16.3	43.1	67.8	64.3
10.0	52.2	56.7	54.2	25.9	61.7	81.0	79.8
20.0	75.4	77.2	76.4	40.5	81.0	91.4	90.7
50.0	97.0	97.2	95.4	71.2	97.5	98.9	99.0

Table 6.18. Unit area yields of sediments and nutrients for the period of record, average gross erosion rates, and average sediment delivery percentages for three northwestern Ohio watersheds. Data through the 1985 water year.

	Average Gross Erosion Rate metric tons/ha/yr	Sediment metric tons/ha/yr	Average Sediment Delivery Ratio As Percent	Total Phosphorus kg/ha/yr	Soluble Reactive Phosphorus kg/ha/yr	Nitrate + Nitrite-N kg/ha/yr	Total Kjeldahl Nitrogen kg/ha/yr
Honey Creek	6.86	0.62	9.0	1.30	0.22	15.5	5.8
Sandusky R.	8.25	0.83	10.0	1.55	0.29	15.8	5.6
Maumee R.	6.84	0.68	10.0	1.50	0.25	15.6	5.5
Average for agricultural lands				0.50		- - 5.0 - -	

Average gross erosion rates, as calculated during the Lake Erie Wastewater Management Study (Logan et al. 1982) are also listed in Table 6.18. The average gross erosion rates in these watersheds are lower than average gross erosion rates for U.S. cropland. These gross erosion rates listed in Table 6.18 probably slightly overestimate current erosion rates, due to the adoption of various types of conservation tillage practices in the Lake Erie Basin. Unfortunately, no new estimates of gross erosion rates for these watersheds are available. Using the LEWMS gross erosion rates, the delivery ratios for sediments average about 10%. Sediment delivery ratio estimates for other Lake Erie Basin watersheds have been described by Baker (1984) and Baker et al. (1985b).

6.2.7. Comparisons of Agricultural Nonpoint Pollution in the Lake Erie Basin and the Chesapeake Basin

The large magnitude of agricultural pollution in the Lake Erie Basin is evident when compared to data from the Chesapeake Bay Region (Macknis 1985, Smullen et al. 1982). While the populations of both areas are the same, the drainage area of Chesapeake Bay is approximately three times larger than that of Lake Erie (Table 6.19). River loadings of sediment, total phosphorus and total nitrogen are, however, much larger for Lake Erie tributaries. Consequently, the unit area loads of sediment, total phosphorus and total nitrogen are 6.4, 5.2 and 4.2 times higher, respectively, than those for Chesapeake Bay watersheds. These higher unit area loads for Lake Erie watersheds are associated with the larger propotions of intensive row crop agriculture in the Lake Erie watershed than in the Chesapeake Basin. The higher population densities coupled with intensive agricultural land use put particularly heavy pressure on the water and soil resources of the Lake Erie Basin.

Table 6.19. Comparison of the Lake Erie Basin and Chesapeake Bay Basin with respect to population, drainage areas and tributary pollutant loads.

Parameter	Lake Erie Basin	Chesapeake Bay Basin
Population	14,000,000	14,000,000
Land Area, km^2	56,980	165,800
River Sediment Loads		
metric tons/yr	6,531,000	3,005,800
kg/ha/yr	1,150	181
River Phosphorus Loads		
metric tons/yr	8,400	4,659
kg/ha/yr	1.47	0.28
River Nitrogen Loads		
metric tons/yr	111,670	77,584
kg/ha/yr	19.6	4.67

SECTION 7

RESULTS AND DISCUSSION: PESTICIDES

7.1. BACKGROUND ON THE PESTICIDE MONITORING PROGRAM IN THE LAKE ERIE BASIN TRIBUTARIES

The pesticide monitoring program in Lake Erie tributaries was initiated in 1980 in response to concerns that conservation tillage could aggravate the pesticide problems in surface waters. An obvious question arose as to the nature of the "pesticide problems" that might be aggravated. Most pesticide monitoring programs in surface waters were directed toward confirming the disappearance of organochlorine insecticides, such as DDT, that had been banned because of their persistence and their tendency to bioaccumulate. Since the pesticides that were replacing them were generally less persistent and often had less of a tendency to bioaccumulate, little priority was given to monitoring their occurrence in surface water and groundwater. Yet it was these newer generation pesticides whose use might be increased with increasing adoption of conservation tillage. Furthermore, the use of many of these compounds, especially the herbicides, had already increased dramatically in association with conventional tillage. According to Hileman (1982) herbicide use in the United States increased 280% between 1966 and 1981.

As our pesticide monitoring program developed, we decided to focus on as many of the "large use" and "local use" compounds as possible, subject to their suitability for inclusion within a multi-residue scanning method using capillary gas chromatography and nitrogen-phosphorus detectors. Considerable analytical method development has accompanied this program and the methods are still undergoing annual modifications. The methods as applied in 1985 included analyses for 19 compounds representing, by weight, about 90% of the herbicides used in Ohio and also 90% of the insecticides.

A second important aspect of the program is that it focuses the sampling effort on runoff events following pesticide application in the spring and summer period (April 15 through August 15). The sampling program outside of the above dates is reduced to about one or two samples per month.

Pesticide monitoring programs for streams and rivers have seldom been focused as described above (General Accounting Office 1981). In the short period of five years, the pesticide monitoring data set for Lake Erie tributaries has become the largest data set of its kind available in the United States. Because studies of comparable detail and duration are virtually nonexistent, data with which to directly compare the Lake Erie Basin data are generally not available. Recent studies of exposure patterns for alachlor (U.S. EPA 1986) and atrazine (Ciba-Geigy 1986) do provide some basis for comparisons with other regions. Most of the discussion and analyses will involve comparisons from within the data set rather than with other regions.

7.2. PESTICIDE CONCENTRATIONS IN LAKE ERIE TRIBUTARIES

7.2.1. Chemograph Patterns

In Figures 7.1-7.12 the runoff patterns for 1982-1985 of four major herbicides (atrazine, alachlor, metolachlor and cyanazine) are illustrated for Honey Creek, the Sandusky River and the Maumee River. The corresponding hydrographs and nitrate chemographs are also shown for each year and station. The graphs are restricted to the April 15 through August 15 period since that time interval encompasses the major periods of pesticide runoff. With few exceptions (e.g., atrazine and metolachlor), the concentrations of pesticides outside of this time interval are near or below the detection limits. Atrazine and, to a lesser extent metolachlor, is present in concentrations well above detection limits for much of the year, particularly during runoff events. In Figure 7.1-7.12 the concentration scales for pesticides and nitrates are uniform for all years and stations, so that the concentration curves for a given parameter are directly comparable in all of the plots. None of the data in the graphs have been corrected for recoveries less than 100%.

The data presented in Figures 7.1-7.12 suggest that pesticide runoff in these tributaries has the following characteristics:

1. Pesticide concentrations during late April and early May are below or near detection limits.

2. Pesticide concentrations increase in association with runoff events.

3. The peak pesticide concentrations can occur in late May, June, or July. Some of the highest pesticide concentrations observed occurred in July, suggesting that hydrological factors have a greater influence on pesticide concentrations than pesticide breakdown in the soil (see Honey Creek 1984, Figure 7.3). A rainfall event of a particular intensity and duration can yield high stream concentrations even though the pesticides have been on the fields for some time.

4. By mid August, pesticide concentrations, even in association with runoff events, are low and approach detection limits.

5. Peak pesticide concentrations decrease with increasing watershed size.

6. Multiple storms with high pesticide concentrations can occur in the same watershed in the same year. (See Honey Creek 1985, Figure 7.4). This may contrast with results from field runoff studies, where high pesticide concentrations are generally confined to the first runoff event following pesticide application (Wauchope 1978).

7. The shapes of the pesticide chemograph are rather broad, corresponding more closely to chemographs for nitrates than for sediments. The pesticide chemographs are, however, shifted to the left relative to nitrate chemographs (i.e., they occur earlier in the runoff event). As noted in Section 6.1.2, pesticides probably are exported from fields throughout the

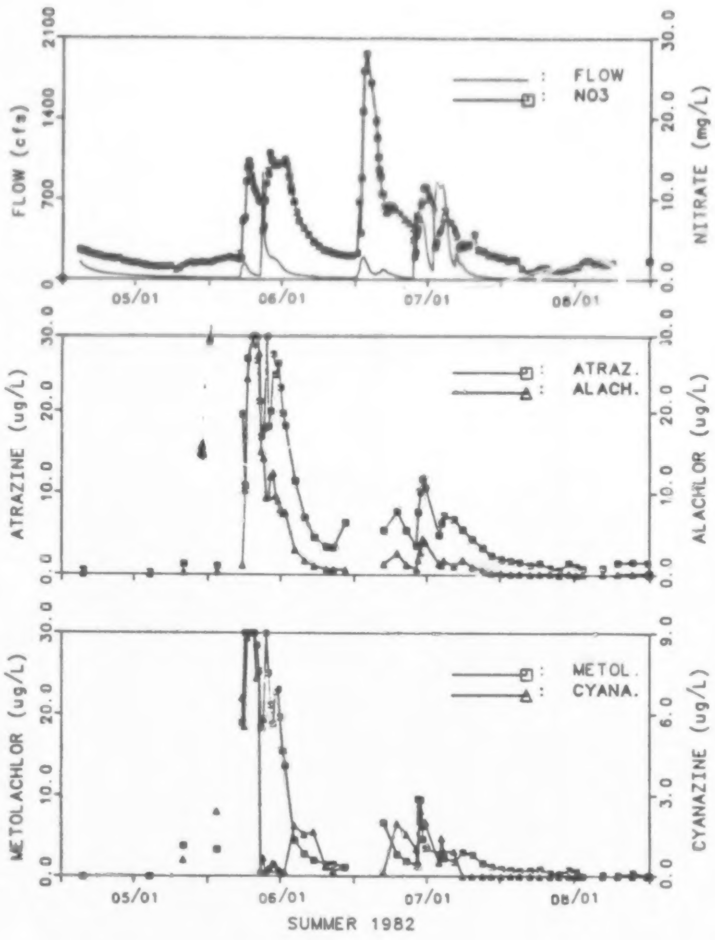

Figure 7.1. Pesticide concentration patterns, discharge and nitrate concentrations in Honey Creek, 1982.

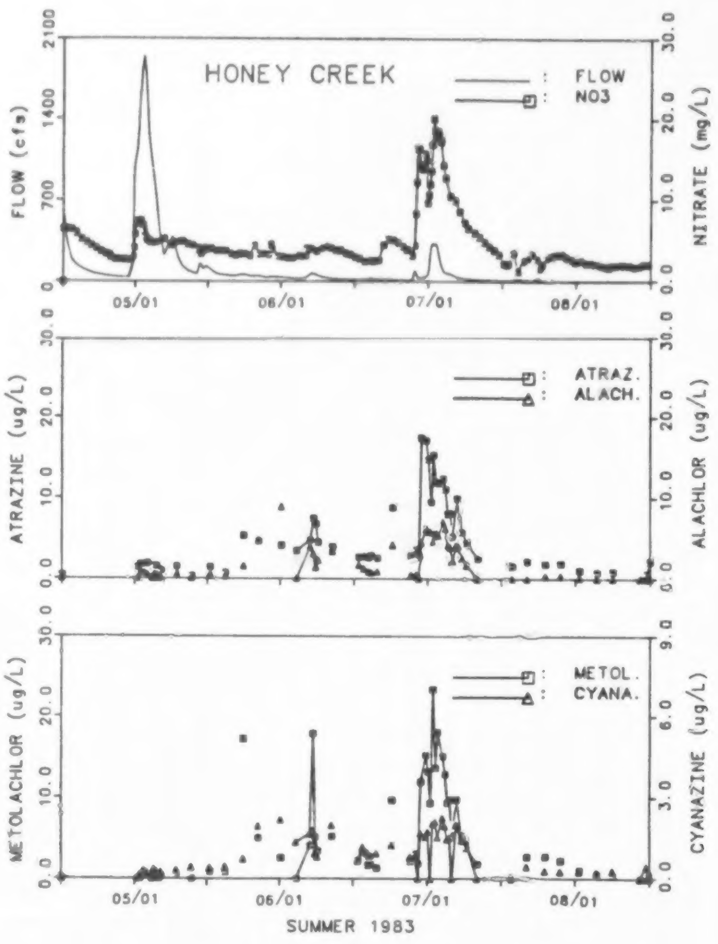

Figure 7.2. Pesticide concentration patterns, discharge and nitrate concentrations in Honey Creek, 1983.

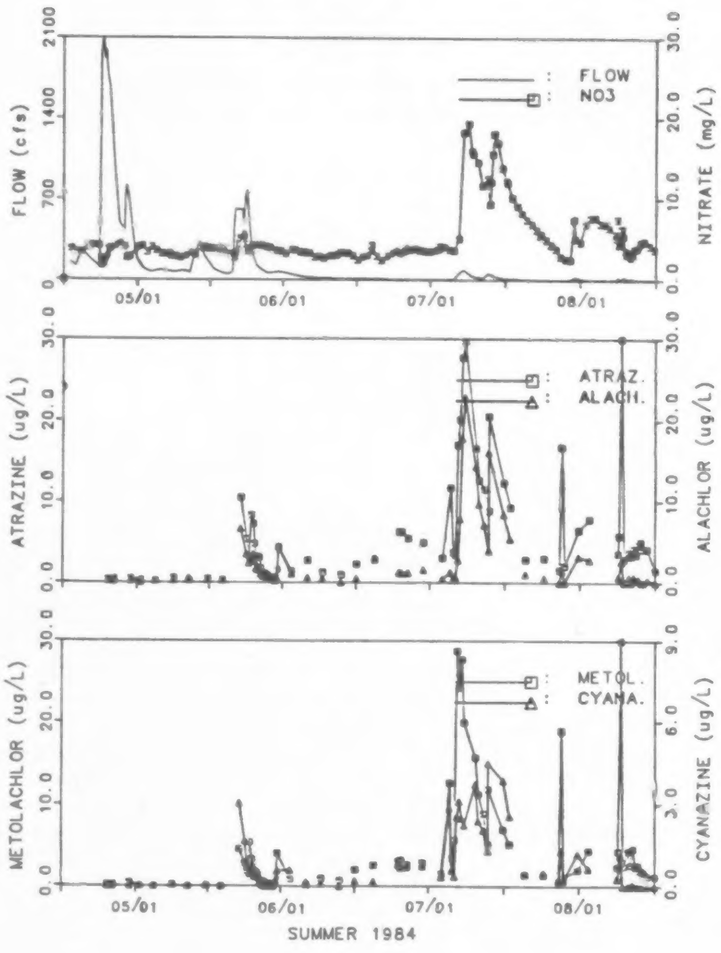

Figure 7.3. Pesticide concentration patterns, discharge and nitrate concentrations in Honey Creek, 1984.

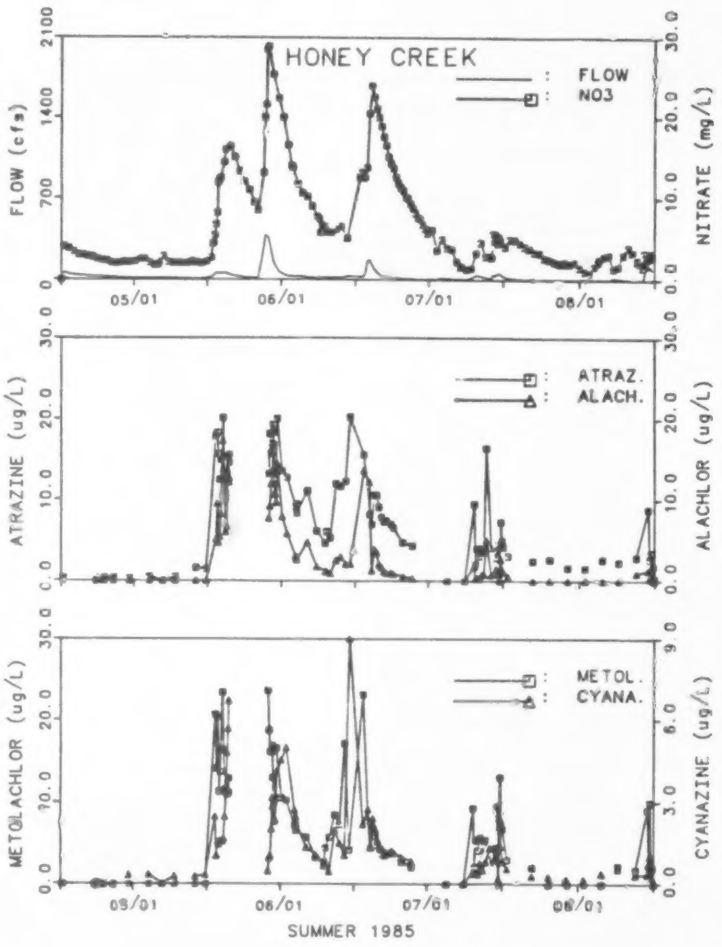

Figure 7.4. Pesticide concentration patterns, discharge and nitrate concentrations in Honey Creek, 1985.

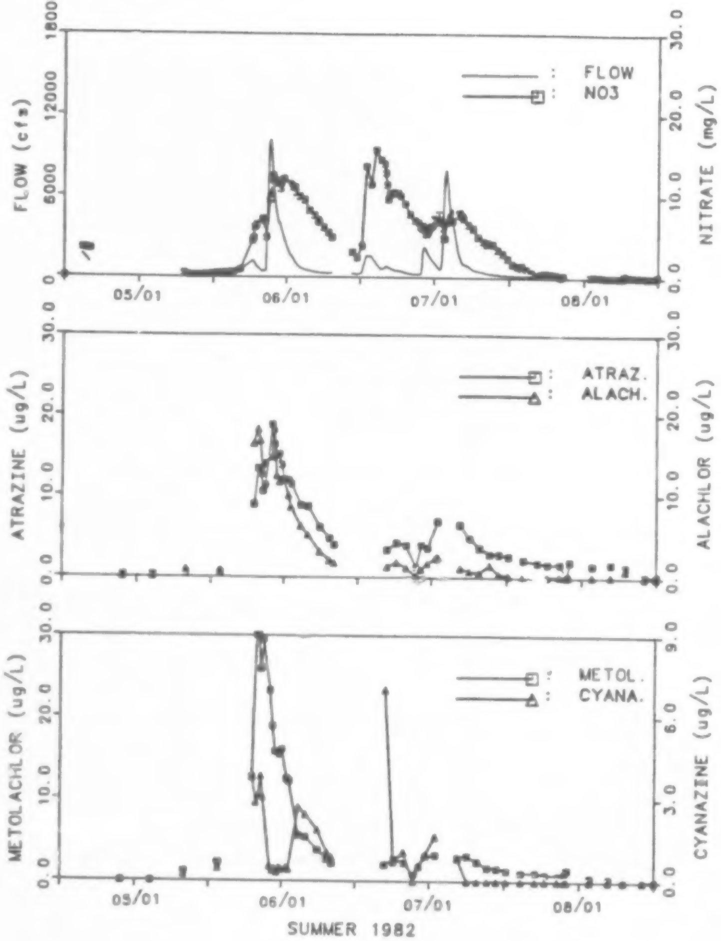

Figure 7.5. Pesticide concentration patterns, discharge and nitrate concentrations in the Sandusky River, 1982.

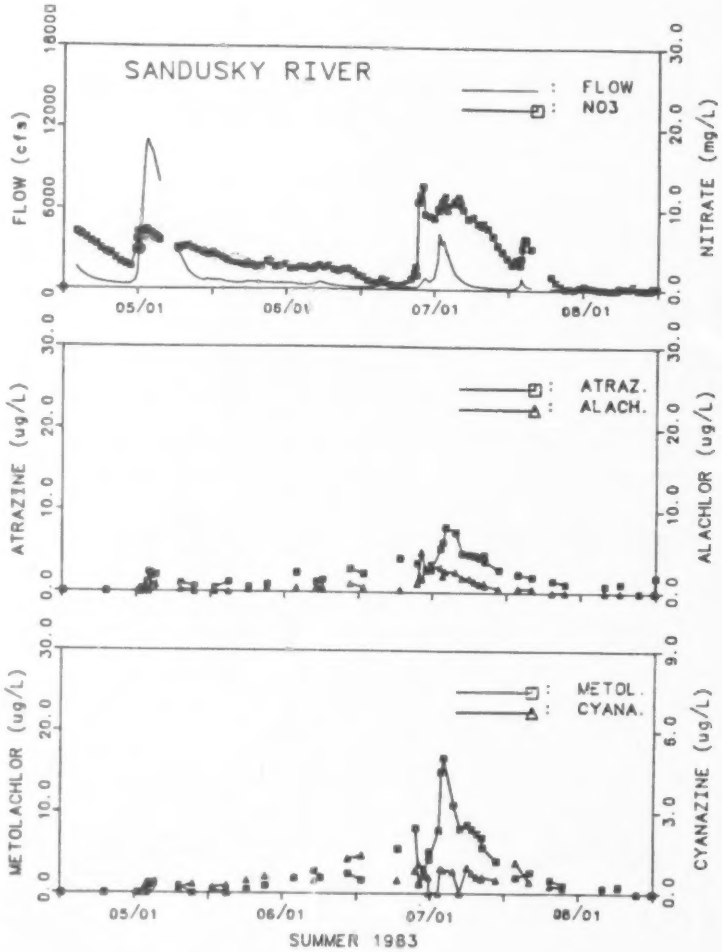

Figure 7.6. Pesticide concentration patterns, discharge and nitrate concentrations in the Sandusky River, 1983.

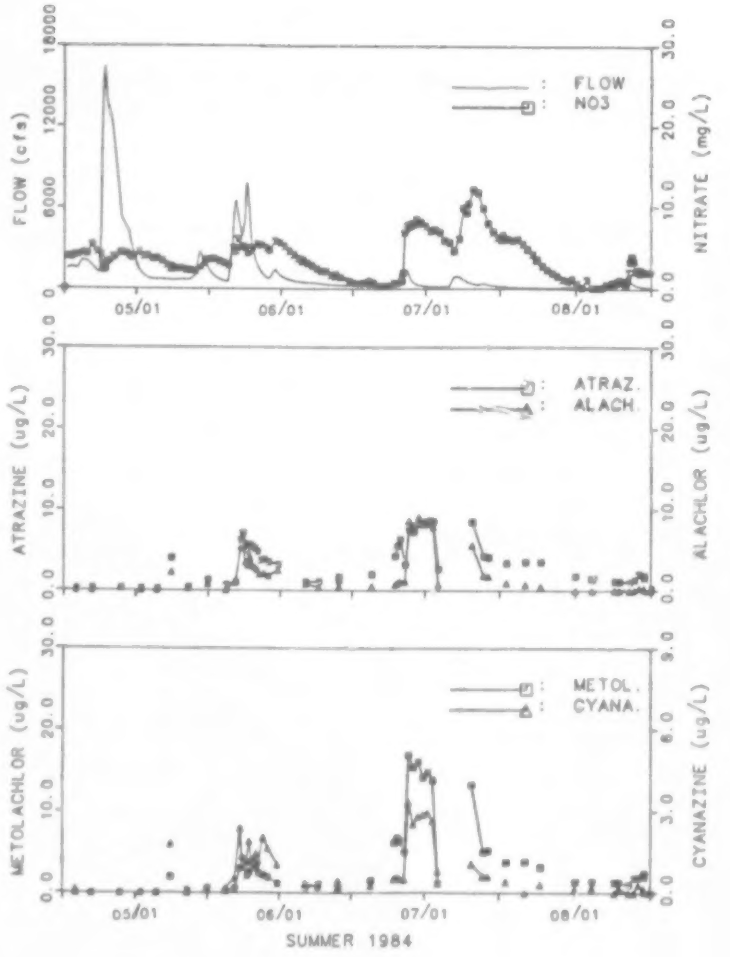

Figure 7.7. Pesticide concentration patterns, discharge and nitrate concentrations in the Sandusky River, 1984.

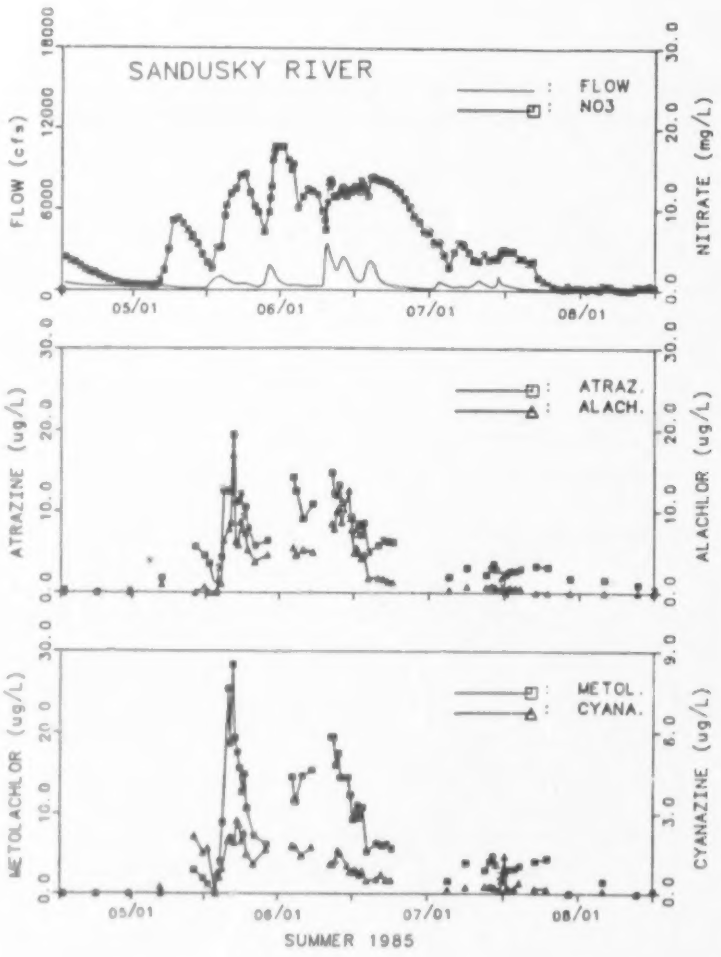

Figure 7.8. Pesticide concentration patterns, discharge and nitrate concentrations in the Sandusky River, 1985.

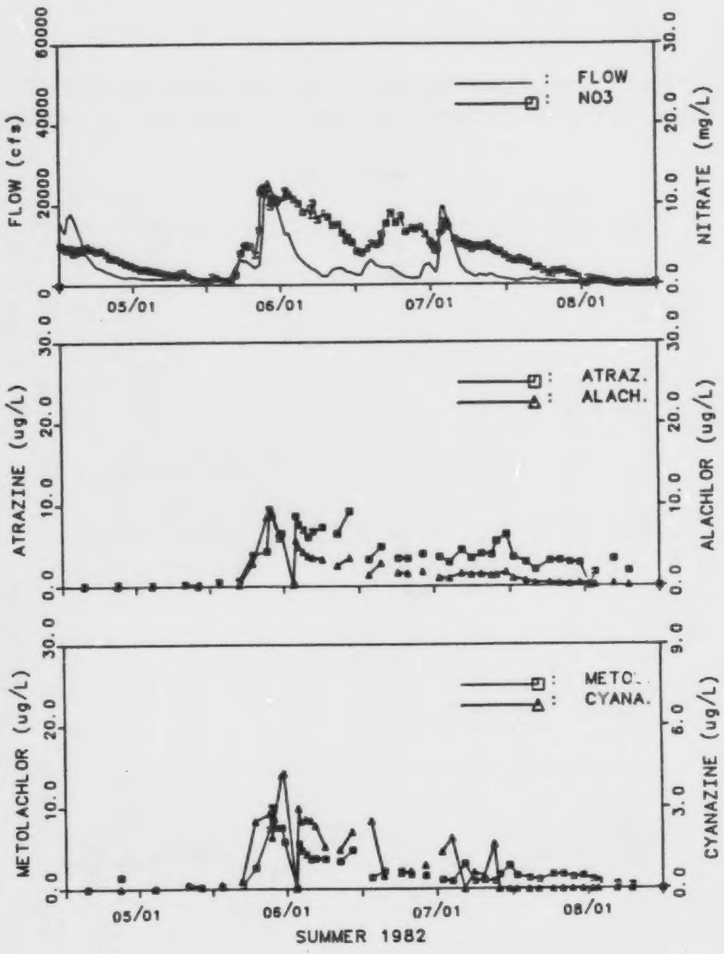

Figure 7.9. Pesticide concentration patterns, discharge and nitrate concentrations in the Maumee River, 1982.

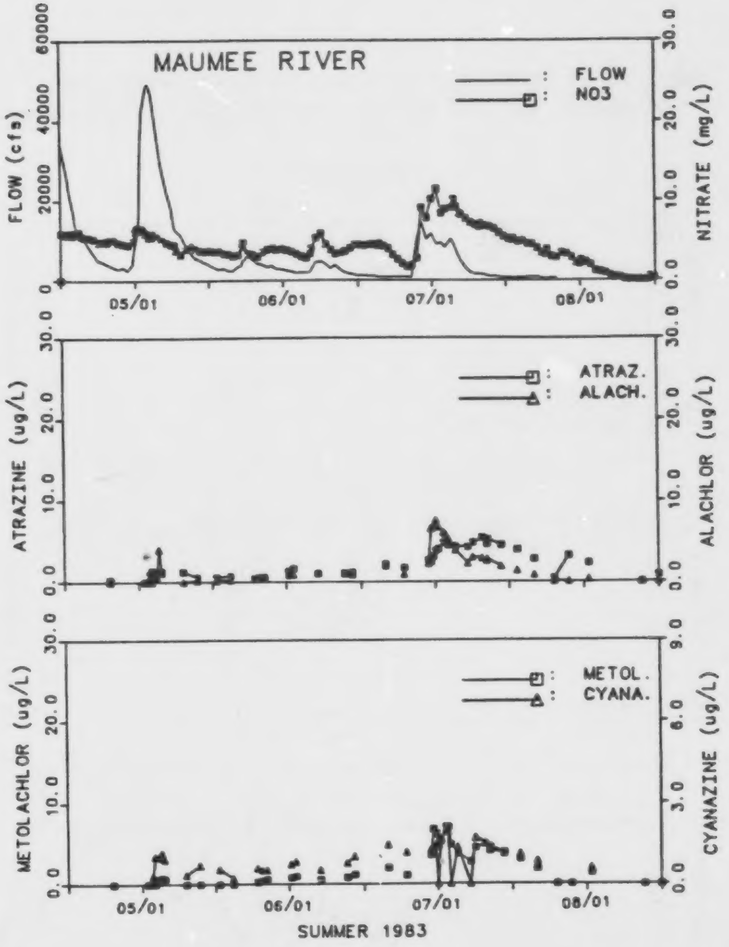

Figure 7.10. Pesticide concentration patterns, discharge and nitrate concentrations in the Maumee River, 1983.

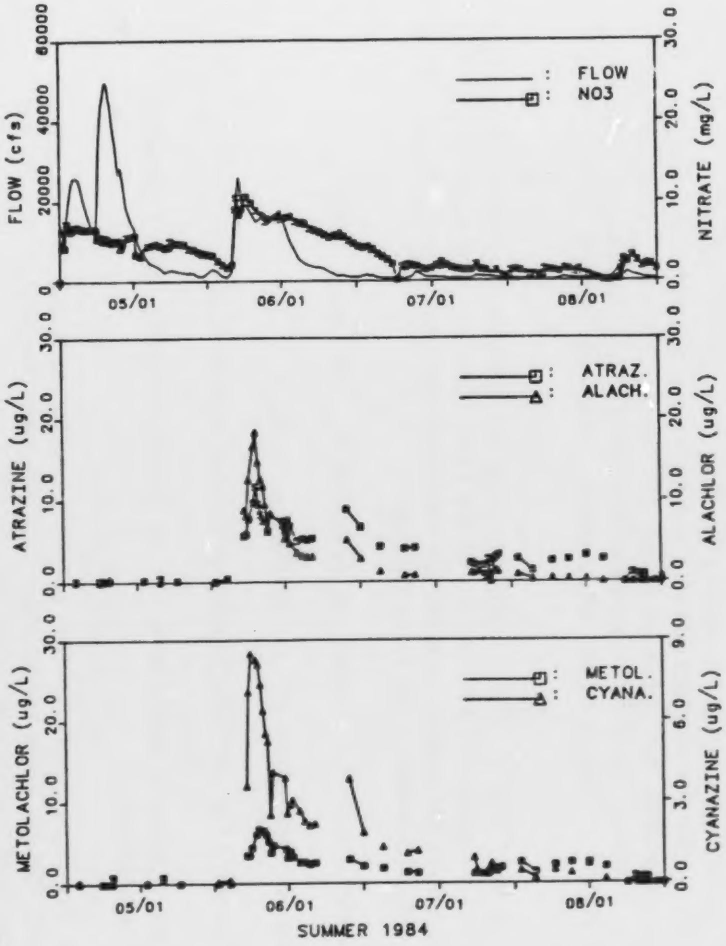

Figure 7.11. Pesticide concentration patterns, discharge and nitrate concentrations in the Maumee River, 1984.

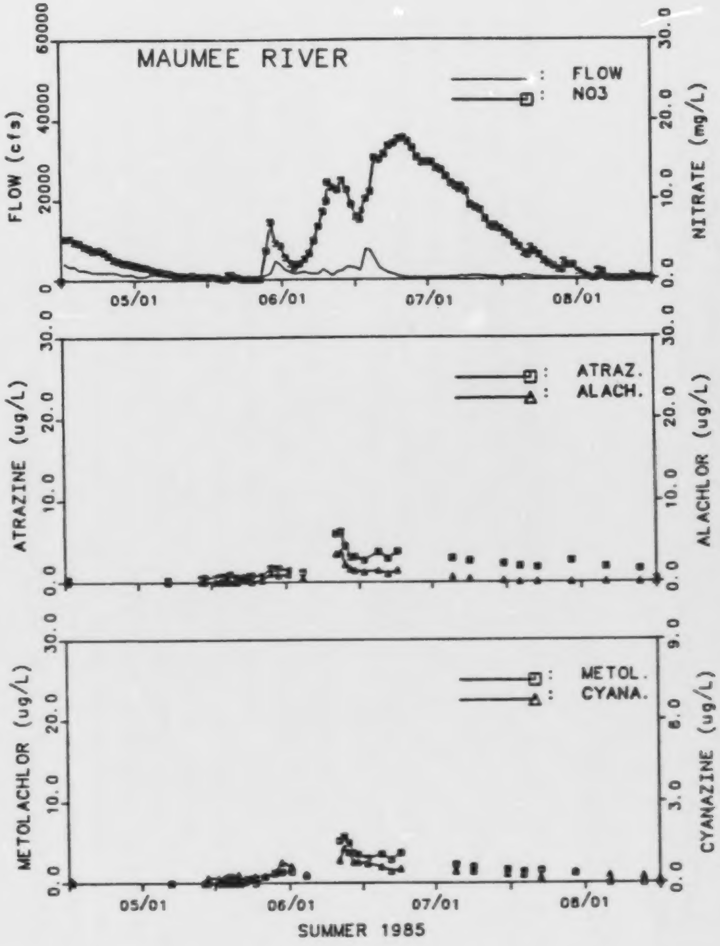

Figure 7.12. Pesticide concentration patterns, discharge and nitrate concentrations in the Maumee River, 1985.

period of surface water runoff, whereas sediment export from fields is focused within the early portions of the surface water runoff and nitrate enters streams via tile drainage and interflow.

7.2.2. Time Weighted Mean Concentrations

The TWMC's for pesticides can be calculated in the same way as for nutrients and sediment (see Section 6.1.5). The output of a program which computes TWMC's for the major pesticides is illustrated in Table 7.1 The program does not incorporate corrections for recoveries less than 100%. In running the program the maximum duration for which any single sample may be used to characterize the stream can be selected. Likewise, the beginning and ending dates for inclusion in the calculation may be selected.

For this report the maximum duration was set at 14 days so that biweekly samples prior to and following the period of maximum concentration would be weighted to a greater extent than the more frequent samples during periods of high concentrations. The time interval was set from April 15 through August 15. These dates cover the same time interval as plotted in Figures 7.1-7.12. The program lists the total number of pesticide samples included in the selected period, as well as the total time interval within the period that was characterized by the sampling program, subject to the limitation set by the maximum duration any single sample was used to characterize the concentration. Tables similar to Table 7.1 are included in Appendix II for each station and year. The pesticide data for 1982 (and 1986) have not yet been transferred into files accessible by the program and are not included in Appendix II.

The program automatically extrapolates the observed TWMC for the selected period to an annual TWMC for that year, using the assumption that the pesticide has zero concentration during the period outside the selected period. Since for several pesticides, the concentrations in the late summer/early fall, while low, are still above detection limits, the above extrapolation to an annual TWMC underestimates the actual values. Techniques for improving the estimated annual TWMC to better reflect actual values are described and utilized in Section 7.2.5.

In Table 7.2 the TWMC's for the major pesticides for the time intervals between April 15 and August 15 are shown for each station for the 1983, 1984 and 1985 water years. The 1984 and 1985 values have been corrected for recoveries less than 100% using the values listed in Table 5.5. It is evident from Table 7.2 that:

1. atrazine, alachlor, metolachlor and cyanazine have the highest TWMC's;
2. there is considerable annual variability in TWMC's;
3. some of the highest TWMC's occur in the smaller watersheds;
4. of the agricultural watersheds, the River Raisin has the lowest pesticide concentrations;
5. the Cuyahoga River, draining primarily forested suburban and industrial areas, has far lower concentrations of the major herbicides than do the agricultural watersheds.

Table 7.1.Pesticide concentrations for the Maumee River in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.503
Results based on 38 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1653	0.0553	19.9206
Carbofuran	0.0461	0.0154	5.55576
Atrazine	1.9017	0.6356	229.164
Terbufos	0.0009	0.0003	.108242
Fonofos	0.0004	0.0001	.503646E-01
Metribuzin	0.2536	0.0848	30.561
Alachlor	0.4723	0.1578	56.908
Linuron	0.0126	0.0042	1.5225
Metolachlor	1.3159	0.4398	158.574
Cyanazine	0.3216	0.1075	38.7578

Table 7.2. Time weighted mean concentrations (μg/L) during the April 15 - August 15 periods for the Michigan and Ohio tributaries to Lake Erie for the years 1983, 1984 and 1985. Data of 1984 and 1985 corrected for recoveries less than 100%.

Year	Maumee River	Sandusky River	Honey Creek	Rock Creek	U. Honey Creek	Lost Creek	River Raisin	Cuyahoga River
Atrazine								
1983	1.751	1.805	3.029	2.516	0.636	3.768	1.067	0.358
1984	3.464	2.940	5.194	1.084	0.969	6.583	1.128	0.254
1985	2.756	6.406	7.673	5.200	5.366	0.938	2.618	0.640
Alachlor								
1983	1.046	0.508	1.381	0.525	0.287	2.369	0.540	0.090
1984	1.688	1.206	2.042	0.240	0.274	1.657	0.754	0.092
1985	0.738	2.933	3.324	0.882	0.399	0.104	1.603	0.021
Metolachlor								
1983	1.308	2.252	2.989	2.917	0.618	1.483	0.317	0.516
1984	1.819	3.151	3.468	2.513	0.361	0.694	0.514	0.001
1985	1.964	7.200	6.577	9.960	2.136	0.613	1.175	0.160
Cyanazine								
1983	0.622	0.447	0.660	0.221	0.202	0.826	0.341	0.292
1984	1.166	0.494	0.664	0.038	0.152	1.569	0.492	0.006
1985	0.407	0.782	1.466	0.252	3.056	0.567	0.580	0.120
Metribuzin								
1983	0.443	0.296	0.353	0.304	0.159	0.586	0.135	0.174
1984	0.830	0.687	0.502	0.075	0.163	0.457	0.086	0.088
1985	0.390	1.410	1.020	0.882	0.402	0.077	0.232	0.0
Linuron								
1983	0.036	0.088	0.332	0.645	0.027	0.367	0.079	0.090
1984	0.040	0.003	0.052	0.0	0.0	0.0	0.013	0.380
1985	0.016	0.407	0.836	0.860	0.059	0.005	0.540	0.132
Simazine								
1983	0.0	0.0	0.0	0.0	0.001	0.002	0.001	0.034
1984	0.210	0.121	0.059	0.079	0.010	0.050	0.048	0.842
1985	0.223	0.266	0.235	0.079	0.076	0.014	0.254	0.597
Carbofuran								
1983	0.175	0.154	0.105	0.061	0.083	0.066	0.172	0.596
1984	0.211	0.154	0.299	0.143	0.063	0.130	0.032	0.205
1985	0.060	0.241	0.338	0.297	0.154	0.031	0.052	0.056
Terbufos								
1983	0.001	0.0	0.001	0.0	0.001	0.036	0.028	0.096
1984	<0.001	0.0	0.0	0.0	0.0	0.0	0.0	0.007
1985	0.002	0.002	0.005	0.002	<0.001	<0.001	0.0	0.0
Fonofos								
1983	0.0	0.004	0.0	0.0	0.002	0.002	0.003	0.167
1984	0.004	0.0	0.0	0.0	0.0	0.003	0.034	0.014
1985	0.001	0.008	0.002	<0.001	0.0	0.0	0.012	0.026

7.2.3. Peak Pesticide Concentrations and Watershed Size

In Table 7.3 the peak pesticide concentrations observed at each station for the 1982-1985 water years are listed. Atrazine has been observed in the highest concentrations, reaching 245 µg/L in Lost Creek in 1984 and 226 µg/L in Upper Honey Creek in 1985. Metolachlor was observed to reach 154 µg/L in Rock Creek in 1985. Cyanazine was found at 86 µg/L in Upper Honey Creek in 1985 in the same samples that had atrazine at 226. Linuron was observed in Lost Creek at 160 µg/L in 1982. Since this value for linuron is more than an order of magnitude higher than any other observations of linuron, it may be a consequence of a spill or other "point source" introduction of linuron rather than runoff from normal field operations.

The data on peak concentrations indicate that higher concentrations are found in the streams having smaller watersheds. It should be noted that the sampling program for pesticides is more likely to hit peak concentrations for large streams, having two collections per day, than it is to hit peak concentrations in small watersheds where a maximum of four samples per day are collected. Thus, as the title to Table 7.3 indicates the peak observed concentrations are listed. It is likely that the values listed in Table 7.3 actually underestimate the real peak values, due to the limitations of the sampling program, and that the underestimates are larger for the smaller watersheds.

Additional scrutiny of the values for peak concentrations presented in Table 7.3 is warranted. As noted for linuron, some of the peak values may be a consequence of spills or improper pesticide handling (e.g., rinsing spray tanks into streams) rather than from field runoff. Examination of adjacent samples and other parameters would help to distinguish spills from field runoff. Since the peak values represent the extremes, the performance of the analytical systems and confirming columns also needs close scrutiny.

It is evident from these studies that the peak concentrations for several of the herbicides are sufficiently high that biological effects would be expected. Krieger (1986b) recently reviewed literature on the biological effects of pesticides and noted the overlap between pesticide concentrations which occur in Lake Erie tributaries and wetlands and concentrations which have been noted to affect biological communities.

7.2.4. Concentration Exceedency Curves

In assessing potential effects of pesticide concentrations on either human or on aquatic ecosystems neither peak concentrations nor TWMC are totally adequate. Information on the duration of exposures to various concentrations allows a better assessment of potential human health or ecosystem level effects. Consequently, the modeling efforts supported by the U.S. EPA's Environmental Research Laboratory at Athens, Georgia attempt to first generate chemographs of the type shown in Figures 7.1-7.12 and then to generate concentration exceedency curves that can be compared with toxicity curves as shown in Figure 7.13 (Donigian et al. 1983). The duration of times a particular pollutant falls within the acute, chronic and subchronic (below maximum acceptable toxicant concentration) ranges can then be assessed.

In Figure 7.14 concentration exceedency curves for the six major herbicides are plotted for each of the eight Lake Erie tributary monitoring stations. The data used for the exceedency plots include the April 15-August 15 periods for 1983, 1984 and 1985. The total number of samples and the total number of days monitored for each station, using a maximum duration for each sample of either 14 days or four days, are listed in Table 7.4. For the exceedency curves, a 14-day maximum was chosen so that the 100% duration would represent approximately the same total number of days for all of the stations. All of the herbicide concentrations are plotted on the same scale (20 µg/L maximum) so that the concentrations of various herbicides can be directly compared and so that different stations can also be directly compared. It should be noted that these duration curves only apply to the April 15-August 15 period and hence cover only about one third of the time (see Table 7.4 for the total days covered out of the three-year period). Since most of these herbicides are virtually absent at time periods outside the selected time intervals, the duration curves for the entire period would compress the curves of Figure 7.14 into the left 33% with essentially no exposures during the added 67% of the time.

From viewing exposure duration curves, the following aspects of pesticide concentrations in Lake Erie tributaries are evident.

1. For all of the tributaries atrazine residues are present for the longest duration of time.

2. For Sandusky Basin stations, metolachlor concentrations are higher than atrazine for the short durations with highest pesticide concentrations.

3. For the Maumee River and Lost Creek, alachlor concentrations are higher than atrazine for the short durations with highest pesticide concentrations.

4. In general, as watershed size decreases, herbicide concentrations are higher for the brief, high concentration periods, but drop off more quickly to low concentrations and, except for atrazine, disappear more quickly.

5. The River Raisin, although also dominated by agricultural land use, has, in general, much lower pesticide concentrations than northwestern Ohio tributaries. This may be associated with the more permeable soils in the River Raisin watershed.

6. The Cuyahoga River has very low pesticide concentrations, particularly for the typical corn and soybean herbicides. Only a small proportion of the Cuyahoga Basin is devoted to row crop agriculture.

7. The data suggest that the ratios of alachlor to metolachlor use in Lost Creek and Rock Creek are very different, with Rock Creek having relatively more metolachlor use than Lost Creek.

The differences in concentration duration curves, both in respect to individual compounds and between stations, should provide useful information upon which to evaluate the performance of pesticide runoff models. The shapes of curves reflect combinations of use patterns, decay rates, solubility, soil type, and watershed size.

Table 7.3. Maximum pesticide concentrations (µg/L) observed at river transport stations during the years 1982, 1983, 1984, and 1985. Data of 1984 and 1985 corrected for recoveries less than 100%.

Year	Maumee River	Sandusky River	Honey Creek	Rock Creek	U. Honey Creek	Lost Creek	River Raisin	Cuyahoga River
Atrazine								
1982	14.04	18.76	48.41	- - -	- - -	38.91	9.263	0.742
1983	5.415	7.971	17.48	16.36	8.492	31.44	9.608	1.436
1984	13.62	10.15	37.46	15.55	5.743	245.4	5.893	1.031
1985	9.000	28.42	29.23	48.09	225.9	6.110	10.00	3.010
Alachlor								
1982	9.266	18.20	74.99	- - -	- - -	18.46	8.163	0.603
1983	7.485	4.924	8.871	11.88	8.688	34.44	8.522	1.164
1984	17.64	8.754	22.01	7.137	0.817	31.84	4.837	0.336
1985	5.640	26.31	27.06	20.19	2.250	1.610	8.760	0.380
Metolachlor								
1982	10.06	40.64	90.80	- - -	- - -	12.71	3.317	0.733
1983	7.033	16.70	23.42	66.50	29.02	13.28	4.586	5.683
1984	13.73	19.45	35.42	57.15	2.145	7.894	4.313	0.0
1985	8.520	42.40	35.00	154.0	25.10	6.260	7.120	0.850
Cyanazine								
1982	4.260	6.993	14.88	- - -	- - -	10.08	4.288	6.618
1983	1.942	1.392	2.231	1.495	1.336	10.25	2.667	1.357
1984	10.16	3.401	4.984	1.179	0.857	23.09	3.823	0.085
1985	1.580	3.440	8.500	2.830	86.10	2.510	2.270	0.540
Metribuzin								
1982	3.356	8.208	8.241	- - -	- - -	5.418	1.726	0.526
1983	4.200	2.447	3.423	4.885	6.937	6.940	2.456	1.050
1984	10.69	8.085	6.319	0.713	0.730	5.731	0.761	0.204
1985	2.530	4.750	7.350	24.53	3.020	2.030	1.690	0.038
Linuron								
1982	2.324	3.513	13.12	- - -	- - -	159.9	2.788	7.683
1983	0.390	1.029	4.300	7.655	1.220	4.122	0.973	10.93
1984	1.379	0.421	1.930	0.0	0.0	0.0	0.448	2.692
1985	0.420	3.860	5.910	14.16	3.890	0.360	2.410	6.310
Simazine								
1982	6.926	3.355	3.603	- - -	- - -	3.278	4.952	10.77
1983	0.0	0.005	0.0	0.0	0.015	0.078	0.022	0.429
1984	0.781	1.424	1.197	0.830	0.102	0.407	0.244	2.875
1985	0.840	1.320	0.650	0.590	1.180	0.061	0.730	1.810
Carbofuran								
1982	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
1983	0.478	0.500	0.425	0.226	0.569	0.545	0.582	1.976
1984	2.717	1.588	5.747	6.036	1.634	4.054	0.565	1.454
1985	0.760	1.610	3.120	4.770	2.440	0.640	0.390	0.880
Terbufos								
1982	2.250	0.104	1.338	- - -	- - -	0.090	0.127	0.058
1983	0.030	0.0	0.016	0.012	0.047	0.483	0.341	1.057
1984	0.021	0.0	0.0	0.0	0.0	0.0	0.0	0.042
1985	0.019	0.081	0.075	0.044	0.022	0.048	0.0	0.0
Fonofos								
1982	0.215	0.050	0.024	- - -	- - -	0.082	0.205	0.0
1983	0.0	0.033	0.0	0.0	0.030	0.052	0.027	0.810
1984	0.057	0.0	0.0	0.0	0.0	0.060	0.945	0.067
1985	0.024	0.086	0.018	0.0	0.0	0.0	0.091	0.056
Pendimethalin								
1982	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
1983	0.269	0.371	0.623	0.470	3.660	3.455	0.333	1.057
1984	0.666	0.570	1.248	0.276	0.055	0.346	0.080	0.139
1985	0.0	0.130	0.230	0.0	0.0	0.310	0.0	0.0

Table 7.4. Description of data sets used for pesticide concentration exceedency graphs. The data include all samples collected between the April 15 and August 15 periods for the 1983, 1984 and 1985 water years.

River	N	Total Days with 14 day max/sample	Total Days with 4 day max/sample
Maumee R.	165	387	312
Sandusky R.	179	389	325
Honey Cr., Melmore	233	391	340
Rock Cr.	207	381	297
Honey Cr., N. W.	121	390	272
Lost Cr.	127	385	264
Raisin R.	69	366	217
Cuyahoga R.	53	346	171

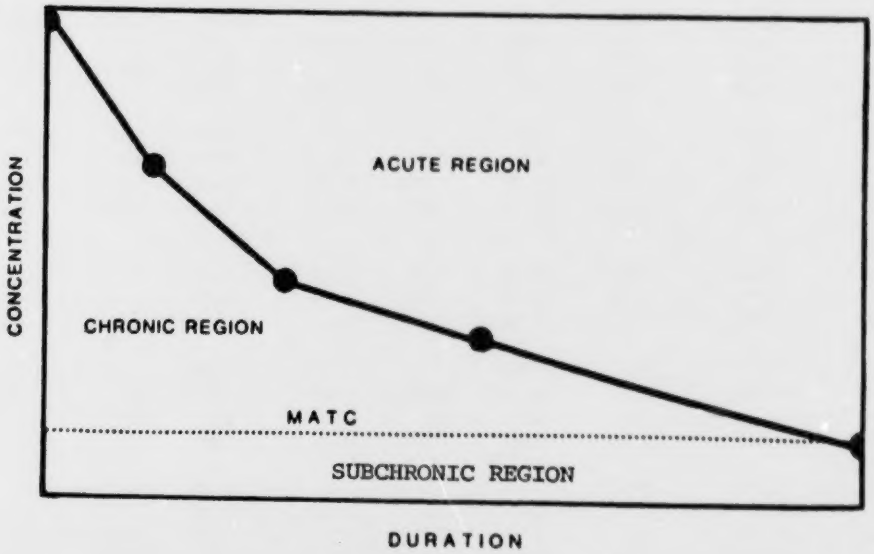

Figure 7.13. Lethality analysis of chemical concentration data. MATC = maximum acceptable toxicant concentration. (After Donigian et al. 1983).

7.2.5. Perspectives on Pesticide Concentration in Lake Erie Tributaries

Two recent studies suggest that the pesticide concentrations in northwestern Ohio tributaries to Lake Erie are particularly high. Ciba-Geiby Corporation recently examined existing data on atrazine concentrations in surface and groundwater (Ciba-Geigy 1986). They utilized data from many sources including internal company monitoring programs and state and federal studies. Only data from areas of significant atrazine use were included in the analysis. Also, only data from fixed interval sampling programs were included, so as to avoid any biases that might be introduced from seasonally stratified sampling programs. This latter restriction excluded data from the Lake Erie tributary monitoring program. The pooled data included 4,000 samples from which the average, the median, the 90th percentile, the 95th percentile and the range were determined. Values below the detection limit were arbitrarily assigned a value of 0.25 μg/L when used to determine average values. These values are shown in Table 7.5.

In order to compare the Lake Erie tributary data with the Ciba-Geigy summaries, we modified the computer program we use to plot the concentration exceedency curves so that the TWMC, the median (50% exceedency), the 90th percentile, the 95th percentile and the range are reported. A sample output from the program is shown in Table 7.6. The program has several options. The maximum time any single sample can be used to represent stream concentrations is selectable. The time interval for data inclusion in the calculation can be selected. Missing time within the selected time can be assigned arbitrary values such as zero or the detection limit or can be ignored.

In Table 7.5, data from Lake Erie tributaries is listed for comparison with the Ciba-Geigy summaries. The programs were run using the selection parameters listed in Table 7.6 (i.e., maximum duration of 14 days, all data from the 1983, 1984 and 1985 water years, and 0.2 μg/L for the unmonitored time period). The data in Table 7.5 have not been corrected for recoveries less than 100%. The data differ from those in Table 7.2 in that in Table 7.5 the values represent annual values whereas in Table 7.2 the values are for the April 15-August 15 period.

The TWMC's for all of the Lake Erie tributaries were slightly higher than the Ciba-Geigy average values. For the larger Lake Erie watersheds, the medians were also higher than the Ciba-Geigy median. The 90th percentiles were higher in four out of six of the northwest rivers, while the 95th percentiles in all of the Lake Erie tributaries were higher than the Ciba-Geigy values. Maximum values for four of the tributaries exceeded the maximum values from the pooled data set. While the Lake Erie values were generally higher than the national averages, the similarity in the values is also very apparent.

In the second recent study, Monsanto Corporation monitored alachlor concentrations in 1985 in raw and finished tap water for 24 municipal water supplies in areas of high alachlor use. The study involved analyses of weekly samples, each of which consisted of weekly composites of seven daily samples. In Table 7.7, the maximum values of the weekly composites are listed for each of the water supplies. The data were also used to estimate an "annualized" mean concentration. Two values are listed for the annualized mean concentration, the lower of which assigns zero concentrations to values less than the detection limits and the higher of which assigns the detection limit (0.20 μg/L) to values lower than the detection limit. The Monsanto study did not include any of the municipal water supplies

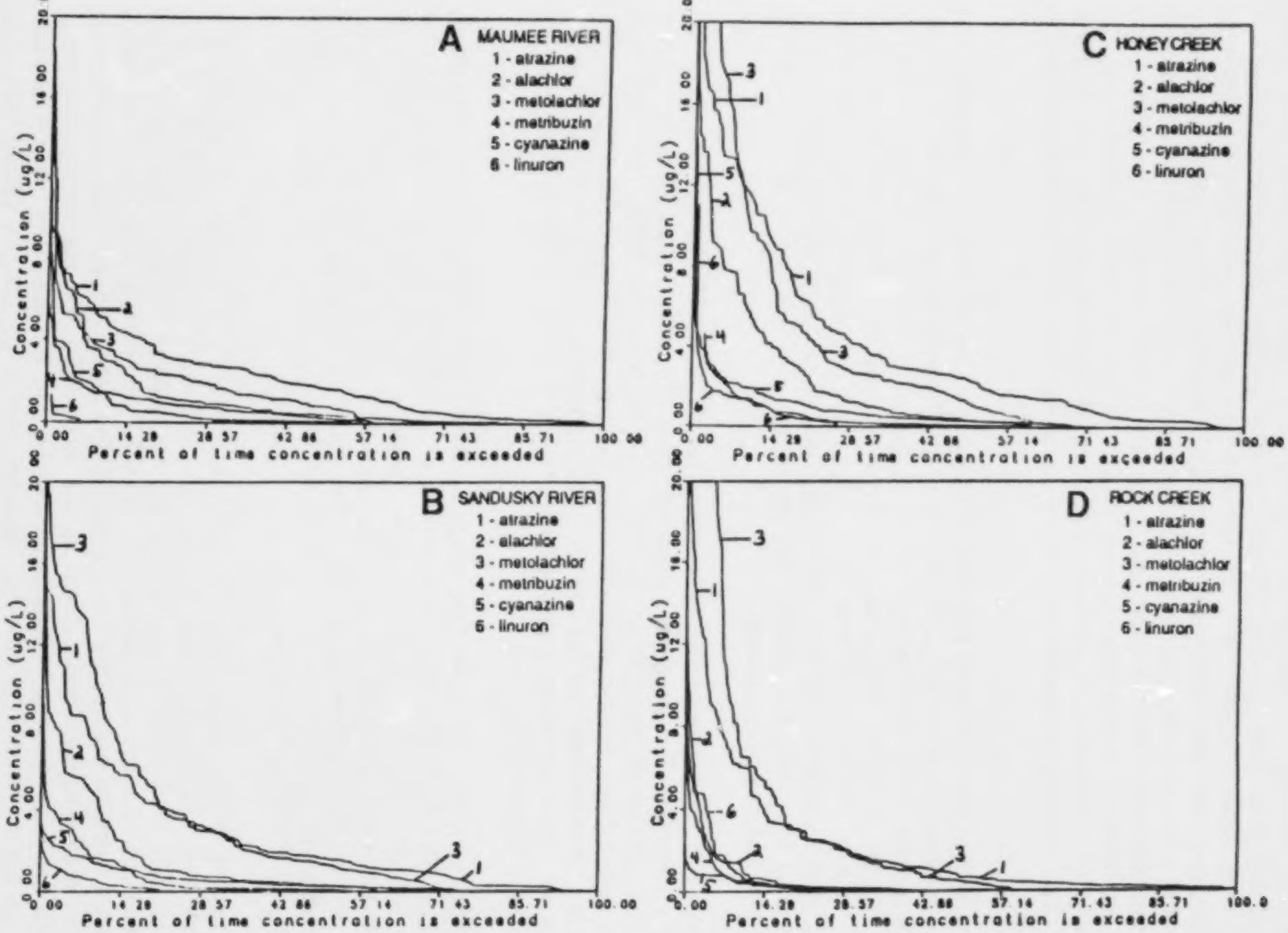

Figure 7.14. Concentration exceedency curves during the April 15-August 15 periods in 1983, 1984 and 1985 for major herbicides at Lake Erie tributary stations. A. Maumee R.; B. Sandusky R.; C. Honey Cr.; D. Rock Cr.; E. Upper Honey Cr.; F. Lost Cr.; G. River Raisin; H. Cuyahoga R.

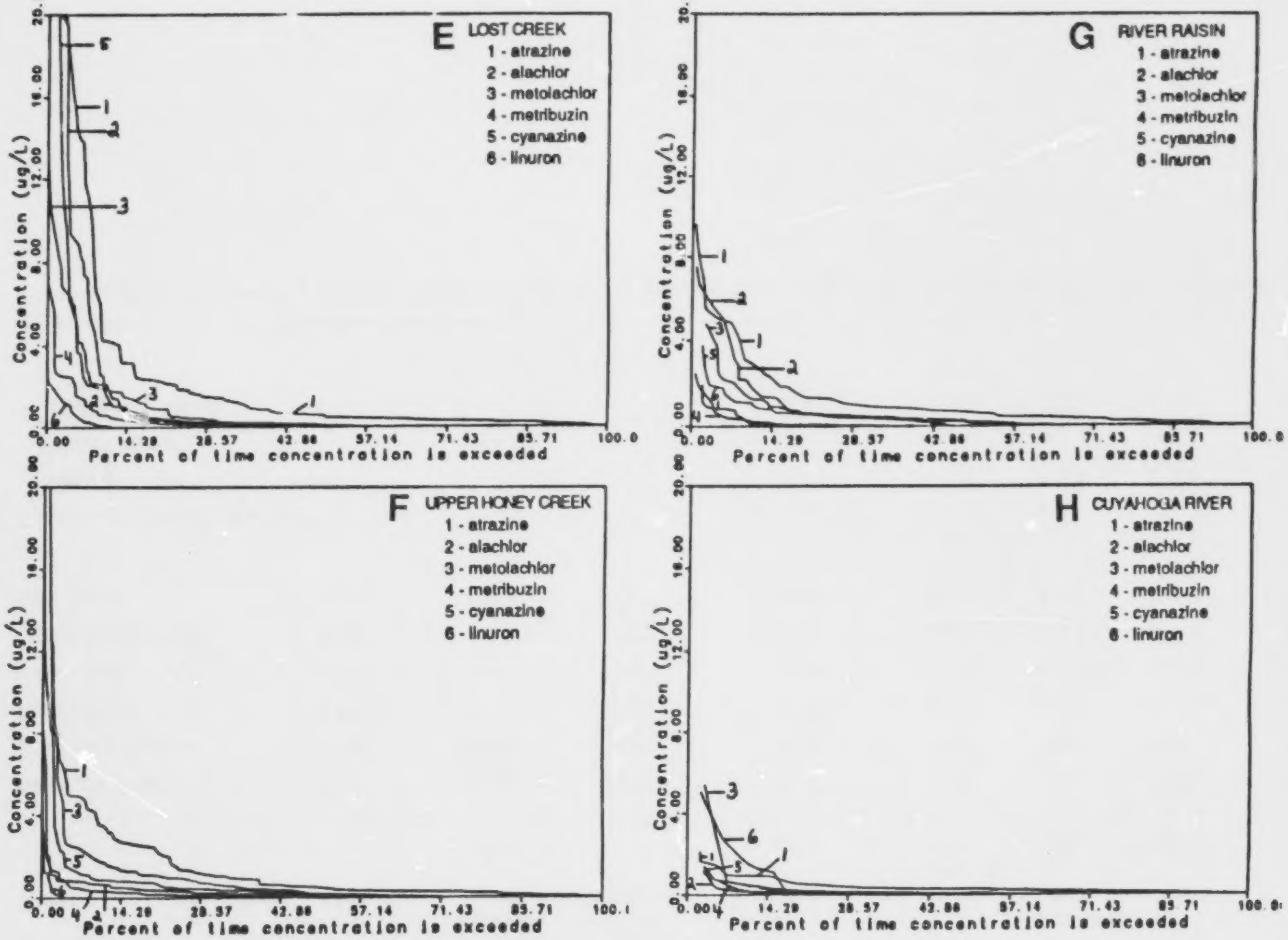

Figure 7.14. Continued.

Table 7.5. Comparison of atrazine concentrations in northwestern Ohio tributaries with preliminary data supplied by the Ciba-Geigy Corporation on atrazine concentrations in surface and ground water for areas of atrazine use. The WQL data are not corrected for recovery.

River	N	Elapsed Time Days	Percent Monitored	TWMC µg/L	Percentile 50th (median) µg/L	90th µg/L	95th µg/L	Range µg/L
Maumee River	206	895	69%	1.70	0.36	2.97	4.54	0-11.7
Sandusky River	219	902	71%	2.00	0.37	3.87	6.22	0-19.46
Honey Creek	289	894	70%	3.05	0.52	5.51	11.14	0-32.2
Rock Creek	272	895	69%	1.49	<0.25	2.48	5.62	0-33.2
Upper Honey Creek	174	895	70%	1.25	<0.25	2.02	3.45	0-56.9
Lost Creek	171	902	70%	2.43	<0.25	2.15	4.03	0-211
Ciba-Geigy Preliminary Data[1]								
Surface Water	4000			1.04	<0.25	2.25	3.75	<0.25-25
Ground Water (Sensitive Areas)	987			0.49	<0.25	0.25	1.25	<0.25-19.7

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[1] Data supplied via personal communications with Dr. Darryl Sumner, Ciba-Geigy Corporation, Greensboro, N.C. on February 11, 1987.

Figure 7.6. Example of tabular output produced along with pesticide concentration exceedency plots.

```
River: MAUMEE               Pesticide: Alachlor


Total number of samples:                          206
Initial sample used: 8304041455
Final sample used:   8509161500
Elapsed time between initial and final samples:   896.004 days
Total time represented by samples:                631.032 days
Time not represented by samples:                  264.972 days
Maximum time a sample represents:                  14.000 days



DISTRIBUTION CHARACTERISTICS OF TIME-WEIGHTED CONCENTRATIONS
  All concentrations are given in micrograms per liter

Time-weighted mean concentration:         0.742
Median concentration (50% percentile):    0.200 (at 48.81th percentile)
90th percentile concentration:            1.085 (at 89.45th percentile)
95th percentile concentration:            2.859 (at 94.70th percentile)
Minimum concentration:                    0.000
Maximum concentration:                   18.350


Conditions imposed on this run:
  Data used:  data between 8304041455 and 8509161500
  Handling of missing time: missing time assigned a concentration of .2
```

Table 7.7. Weekly maximum and annual mean concentrations of alachlor in raw and finished surface water for the 1985 growing season.[1]

		Alachlor Concentration (µg/L)			
		Weekly Maximum		Annualized Mean	
Location	State	Raw	Finished	Raw	Finished
Bethany	MO	<0.20	<0.20	0-0.20	0-0.20
Blanchester	OH	1.3	1.1	0.16-0.32	0.15-0.31
Breese	IL	4.6	4.4	0.29-0.44	0.29-0.42
Charleston	IL	<0.20	<0.20	0-0.20	0-0.20
Clarinda	IA	<0.20	<0.20	0-0.20	0-0.20
Columbus	OH	10.7	10.9	1.3 -1.5	1.3 -1.4
Davenport	IA	0.68	0.32	0.02-0.21	0.01-0.20
Decatur	IL	<0.20	0.29	0-0.20	0.03-0.20
Greenville	NC	0.26	0.27	0.01-0.20	0.01-0.20
Kankakee	IL	0.85	0.77	0.09-0.24	0.08-0.24
Lexington	MO	0.84	0.59	0.05-0.23	0.03-0.21
Marion	IL	<0.20	<0.20	0-0.20	0-0.20
Michigan City	IN	<0.20	<0.20	0-0.20	0-0.20
Monroe	MI	<0.20	<0.20	0-0.20	0-0.20
Mount Vernon	IN	1.1	1.0	0.06-0.24	0.05-0.23
Muncie	IN	2.5	2.8	0.26-0.40	0.25-0.38
Piqua	OH	0.89	0.63	0.05-0.23	0.04-0.22
Quincy	IL	0.54	0.70	0.04-0.21	0.06-0.23
Richmond	IN	3.5	3.6	0.57-0.68	0.57-0.69
Roanoke Rapids	NC	<0.20	<0.20	0-0.20	0-0.20
Toledo	OH	<0.20	<0.20	0-0.20	0-0.20
University of Iowa	IA	1.6	1.8	0.10-0.28	0.11-0.29
Wyaconda	MO	0.24	<0.20	0.02-0.20	0-0.20
Ypsilanti	MI	<0.20	<0.20	0-0.20	0-0.20
Overall		10.7	10.9	0.13-0.31	0.12-0.30

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[1] Reference: Monsanto, 1986 as cited by U.S. EPA, 1986 (Alachlor Special Review Technical Support Document Sept. 1986, Office of Pesticide Programs. U.S. EPA).

located along the Sandusky or Maumee rivers.

In the Monsanto study, the highest weekly maximum and the highest annualized mean concentrations of alachlor were observed in Columbus, Ohio. The Scioto River watershed, which supplies much of the water for the city of Columbus, is very similar to the Maumee and Sandusky watersheds with respect to both land use and soil types. The Monsanto study also clearly shows that conventional water treatment does not remove alachlor to any appreciable extent, since raw water and finished water had essentially the same concentrations. Similar results have been observed for water treatment plants along the Sandusky and Maumee rivers (Baker 1983d).

In Table 7.8 alachlor concentration data for the Lake Erie tributaries are summarized in the same format as the atrazine data of Table 7.5. For these calculations a value of 0.20 µg/L was assigned to all missing time for the calculation period. Samples with values less than 0.20 µg/L were still allowed to represent their associated time intervals. The data in Table 7.8 have not been corrected for recoveries less than 100%., The above calculational procedures for Lake Erie tributaries would tend to yield concentrations biased low relative to the Monsanto values listed in Table 7.7. Nevertheless, the TWMC's for Lake Erie tributaries, which would correspond to the annualized mean concentrations of the Monsanto data, are high in comparison to the locations included in the Monsanto study. Only the Columbus, Ohio and the Richmond, Indiana locations had mean concentrations in the same range as those of the larger Lake Erie tributaries. The weekly maximum values of the Monsanto study would correspond approximately to the 98th percentile. For the major Lake Erie tributaries the 95th percentile concentrations of alachlor are higher than the weekly maximum values in the Monsanto study.

The above comparisons do suggest that the pesticide concentrations observed in Lake Erie tributaries are higher than average for rivers draining agricultural watersheds. The relatively fine textured soils of this region tend to seal rather quickly, resulting in large amounts of surface runoff. These conditions may result in particularly severe runoff of pesticides.

7.3. PESTICIDE LOADING IN LAKE ERIE TRIBUTARIES

7.3.1. Method of Calculating Pesticide Loads

Pesticide loads can be calculated in a manner similar to that used for nutrient and sediments (see Section 6.2.1). Pesticide concentration data are often far more widely spaced in time than nutrient data. Consequently, the flow data associated with the nutrient samples are much more complete than would be flow data associated with pesticide samples. Furthermore, pesticide samples are not necessarily collected at the same time as nutrient samples. For these reasons, a new approach and associated computer programs were developed for estimating pesticide loads from these data.

In developing the pesticide load calculation technique, the general concept of the mid-interval summation approach was retained, but the characterization of a given time interval by pesticide concentration and flow had to be decoupled. The process involves the following steps:

1. Choose a maximum interval of time that pesticide samples will be allowed to represent. This value is used to set up a time window symmetrically about the sample - the time it represents.

2. If the windows of two adjacent samples overlap, the window boundary for both samples is reset to half-way between the two.

3. The resulting time window for a given pesticide sample is imposed on the flow data stored in the nutrient file. Flows corresponding to the edges of the window are calculated by linear interpolation. The total discharge for the time window is calculated by the mid-interval technique, applied to all of the individual flow measurements available within the time window. The load associated with that pesticide sample is then calculated as the product of the pesticide concentration and the total discharge. The sample loads calculated in this way are summed to produce the load estimate for the period of interest.

This approach does not change the basic approach to calculating the load, but allows the more detailed flow data from the nutrient files to be completely utilized, producing a more accurate load estimate.

When concentration data are infrequent in time, the measured load may represent a smaller interval of time than the elapsed time, because many of the individual time windows fail to overlap. For this reason, both the elapsed time and the monitored (i.e. "windowed") time are reported, and discharges are calculated for each, subject to the limitation that no flow observation may count for more than one day. When flow data are adequate but pesticide data are inadequate, it is useful to extrapolate the loads to the total elapsed time by multiplying the observed load by the ratio of the total discharge during that time to the monitored discharge. This adjusted load estimate is reported along with the original estimate, and is also expressed on a unit area basis. All of the above calculations are accomplished by a computer program which generates tabular outputs (e.g., Table 7.9 and Appendix II). Occasionally the flow data in the nutrient files are too infrequent, and the discharge from the nutrient files is less than the discharge from the pesticide files. The latter is calculated with a 14 day time limit instead of the one day time limit. For these cases, the extrapolated loads are less than the observed loads. When the discharge record from the nutrient file covers many fewer days than the elapsed number of days between the selected dates, the extrapolated load may significantly underestimate the actual loads (e.g., Lost Creek in 1984 and 1985). In these cases, the total loads should be adjusted to the USGS discharge for the elapsed time interval. This option has not yet been added to the pesticide load calculation program.

There is little firm basis for the choice of an interval of time for a pesticide sample to represent. Experimentation indicates that, if flow data are adequate and the pesticide sampling program emphasizes high-flow sampling, the adjusted load estimates are not strongly sensitive to the choice of this time interval.

7.3.2. Pesticide Loading Data

The observed pesticide loads for 1983-1985, as calculated by the above procedure, are summarized in Table 7.10. The associated unit area loads are shown in Table 7.11. The

Table 7.8. Means, percentiles and ranges of alachlor concentration in Lake Erie tributaries.

River	N	Elapsed Time	Percent Monitored	TWMC	Percentile			Range
					50th (median)	90th	95th	
		Days		µg/L	µg/L	µg/L	µg/L	µg/L
Maumee River	206	895	69%	0.77	<0.20	1.09	2.86	0.00-18.4
Sandusky River	219	902	71%	0.78	<0.20	1.03	3.45	0.00-17.0
Honey Creek	289	895	70%	1.18	<0.20	1.76	4.73	0.00-22.9
Rock Creek	272	895	69%	0.35	0.00	0.26	0.66	0.00-12.9
Upper Honey Creek	174	895	70%	0.25	0.14	0.40	0.66	0.00-8.69
Lost Creek	171	902	70%	0.97	0.04	0.28	1.04	0.00-34.5
Raisin River	106	902	68%	0.51	0.20	0.54	1.39	0.00-7.52

Table 7.9: Pesticide loads for the Maumee River, USGS04193500, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 52 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	0	0	0
Carbofuran	235.161	249.423	.152134
Atrazine	2373.65	2517.61	1.53559
Terbufos	2.22466	2.35958	.143921E-02
Fonofos	0	0	0
Metribuzin	664.465	704.763	.429865
Alachlor	1948	2066.14	1.26023
Linuron	44.4298	47.1244	.287431E-01
Metolachlor	1678.25	1780.04	1.08572
Cyanazine	1103.59	1170.52	.713948
Pendimethalin	56.8027	60.2476	.367475E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 116.434 days.
The monitored discharge is 681260 cfs-days, or 1667.04 million cubic meters.

The total discharge during this time is 722577 cfs-days, or 1768.14 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 161 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 7.10. Observed pesticide loads, in kilograms, for the Michigan and Ohio tributaries to Lake Erie for the years 1983, 1984 and 1985. See Appendix II Tables.

Year	Maumee River	Sandusky River	Honey Creek	Rock Creek	U. Honey Creek	Lost Creek	River Raisin	Cuyahoga River
Atrazine								
1983	2347.6	563.2	76.61	19.20	6.052	7.766	412.3	73.80
1984	5529.5	764.2	93.94	30.67	1.296	27.67	373.3	63.24
1985	1035.0	1208.3	101.2	14.24	6.809	0.116	220.0	145.7
Alachlor								
1983	1946.8	179.9	31.41	5.474	3.203	5.887	257.3	13.23
1984	4989.1	432.0	45.53	10.51	0.729	3.785	260.5	22.12
1985	404.9	767.5	62.29	2.781	0.709	0.024	136.0	3.79
Metolachlor								
1983	1671.6	635.1	59.58	24.56	2.968	3.113	154.6	85.21
1984	3491.3	603.8	53.42	24.38	1.433	0.985	110.1	9.075
1985	906.0	1521.9	97.19	27.20	3.464	0.035	103.0	35.11
Cyanazine								
1983	1100.6	98.68	12.88	1.385	0.517	1.935	107.6	56.31
1984	2903.5	163.9	13.80	2.055	0.269	3.273	202.7	4.397
1985	170.5	137.1	17.13	0.658	2.713	0.291	45.04	21.53
Metribuzin								
1983	663.7	84.24	8.088	2.894	0.741	1.586	73.58	21.81
1984	3323.2	200.5	14.11	1.669	0.589	1.182	45.95	32.79
1985	189.7	364.5	20.80	3.346	0.664	0.013	21.11	0.466
Linuron								
1983	44.43	26.66	6.434	5.453	0.273	0.595	31.39	12.42
1984	54.30	1.345	0.665	0.0	0.0	0.0	0.458	83.94
1985	24.30	101.2	13.74	2.219	0.165	0.001	32.40	57.26
Simazine								
1983	0.0	0.0	0.0	0.0	0.001	0.005	0.131	4.982
1984	327.02	45.93	2.653	2.972	0.535	0.093	11.74	150.3
1985	89.26	55.61	1.439	0.215	0.130	0.001	17.05	114.5
Carbofuran								
1983	233.19	34.79	2.991	0.266	0.184	0.083	40.16	161.1
1984	564.17	73.83	7.559	6.921	0.513	0.315	3.342	75.02
1985	34.93	48.15	6.504	1.262	0.363	0.014	4.023	21.60
Terbufos								
1983	2.225	0.0	0.007	0.0	0.005	0.052	6.738	14.29
1984	0.693	0.0	0.0	0.0	0.0	0.0	0.0	2.746
1985	0.613	0.658	0.057	0.005	0.001	0.353	0.0	0.0
Fonofos								
1983	0.0	0.141	0.0	0.0	0.001	0.003	0.764	13.86
1984	10.67	0.0	0.0	0.0	0.0	0.007	5.515	4.553
1985	0.908	1.729	0.009	0.001	0.0	0.0	1.027	3.310
Pendimethalin								
1983	56.80	4.154	0.338	0.090	0.036	0.579	8.129	12.01
1984	117.1	5.345	2.455	0.065	0.005	0.033	2.782	0.542
1985	0.0	0.285	0.115	0.0	0.0	0.001	0.0	0.0

Table 7.11. Unit area pesticide loads, in grams per hectare, for the Michigan and Ohio tributaries to Lake Erie for the years 1983, 1984 and 1985. Based on observed loads as presented in Table 7.10.

Year	Maumee River	Sandusky River	Honey Creek	Rock Creek	U. Honey Creek	Lost Creek	River Raisin	Cuyahoga River
Atrazine								
1983	1.432	1.738	1.985	2.182	1.375	8.825	1.528	0.403
1984	3.373	2.359	2.434	3.485	0.295	31.443	1.383	0.345
1985	0.631	3.729	2.622	1.618	1.547	0.132	0.815	0.796
Alachlor								
1983	1.187	0.555	0.814	0.622	0.728	6.690	0.953	0.072
1984	3.043	1.333	1.180	1.194	0.166	4.301	0.965	0.121
1985	0.247	2.369	1.614	0.316	0.161	0.027	0.504	0.021
Metolachlor								
1983	1.020	1.960	1.544	2.791	0.675	3.537	0.573	0.465
1984	2.129	1.864	1.384	2.770	0.326	1.119	0.408	0.050
1985	0.553	4.697	2.518	3.091	0.787	0.040	0.382	0.192
Cyanazine								
1983	0.671	0.305	0.334	0.157	0.117	2.199	0.399	0.308
1984	1.771	0.506	0.358	0.234	0.061	3.719	0.751	0.024
1985	0.104	0.423	0.444	0.075	0.617	0.331	0.167	0.118
Metribuzin								
1983	0.405	0.260	0.210	0.329	0.168	1.802	0.273	0.119
1984	2.027	0.619	0.366	0.190	0.134	1.343	0.170	0.179
1985	0.116	1.125	0.539	0.380	0.151	0.015	0.078	0.003
Linuron								
1983	0.027	0.082	0.167	0.620	0.062	0.676	0.116	0.068
1984	0.033	0.004	0.017	0.000	0.000	0.000	0.002	0.458
1985	0.015	0.312	0.356	0.252	0.038	0.001	0.120	0.313
Simazine								
1983	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.027
1984	0.199	0.142	0.069	0.338	0.122	0.106	0.043	0.821
1985	0.054	0.172	0.037	0.024	0.030	0.001	0.063	0.625
Carbofuran								
1983	0.142	0.107	0.077	0.030	0.042	0.094	0.149	0.880
1984	0.344	0.228	0.196	0.786	0.117	0.358	0.012	0.410
1985	0.021	0.149	0.168	0.143	0.082	0.016	0.015	0.118
Terbufos								
1983	0.001	0.000	0.000	0.000	0.001	0.059	0.025	0.078
1984	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.015
1985	0.000	0.002	0.001	0.000	0.000	0.401	0.000	0.000
Fonofos								
1983	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.076
1984	0.007	0.000	0.000	0.000	0.000	0.008	0.020	0.025
1985	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.018
Pendimethalin								
1983	0.035	0.013	0.009	0.010	0.008	0.658	0.030	0.066
1984	0.071	0.016	0.064	0.007	0.001	0.037	0.010	0.003
1985	0.000	0.000	0.003	0.000	0.000	0.001	0.000	0.000

pesticide loads have considerable annual variability as expected for agricultural chemicals. An important use of data such as these will be to compare export rates with use rates in the study watersheds. A survey of 1986 pesticide usage is currently in progress by Dr. A. C. Waldron of the Ohio State University Extension Service under a grant from the Great Lakes National Program Office. When those data become available, they will be combined with data from a similar survey conducted in 1982. This will allow calculation of the percent of applied pesticide that is exported from large watersheds. The resulting export percentages can be compared with similar data from plot and field size studies and the possible role of instream pesticide processing can be assessed.

7.3.3. Significance of Pesticide Loads

The loadings of most current generation pesticides into Lake Erie, while large in comparison with other toxic substances, also are not viewed as posing priority problems since they are less persistent and have less of a tendency to bioaccumulate than the priority toxic compounds. The major problems that may be associated with the loadings of these compounds relate to resulting concentrations in the bays and wetlands. Although these compounds are not persistent, their continuing large volume use makes them consistent seasonal components of the chemical environment of streams, bays and wetlands.

Surface water export of pesticides generally accounts for a small portion (<1%) of the dissipation/degradation pathways for pesticides applied to cropland. Consequently, the losses of these compounds by surface water runoff are seldom of consequence to farmers.

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APPENDIX 1

NUTRIENT AND SEDIMENT TRANSPORT AT LAKE ERIE TRIBUTARY MONITORING STATIONS: 1982 - 1985 WATER YEARS

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APPENDIX 1 -- NOTES

Contents

This Appendix provides a summary of nutrient and sediment transport data at eight tributary stations in the Lake Erie Basin for the 1982-1985 water years. For each station and water year, the summary consists of an annual hydrograph, a sedigraph and chemographs for total phosphorus, soluble reactive phosphorus, nitrate plus nitrite-nitrogen and specific conductance. Also, on the facing page of each set of graphs, a summary of monthly discharge and monthly sediment and nutrient loads is presented.

Additional Parameters

In addition to the parameters shown in this Appendix, all of the samples have also been analyzed for ammonia nitrogen, total Kjeldahl nitrogen and silica. Chemographs and monthly loading data for these parameters can be obtained from the Water Quality Laboratory, Heidelberg College.

Data Availability

Data containing the concentrations of nutrients and sediments in individual samples are available in the U.S. EPA's STORET data system. The data are stored under the corresponding U.S. Geological Survey station number. Data can also be supplied directly on magnetic tape from the Water Quality Laboratory, Heidelberg College, Tiffin, Ohio 44883.

Pesticide Data (see Appendix 2)

Data on spring runoff of major, currently used herbicides and insecticides are also available for the transport stations, beginning with the 1982 water year. The pesticide data are available in the STORET system or directly from the Water Quality Laboratory.

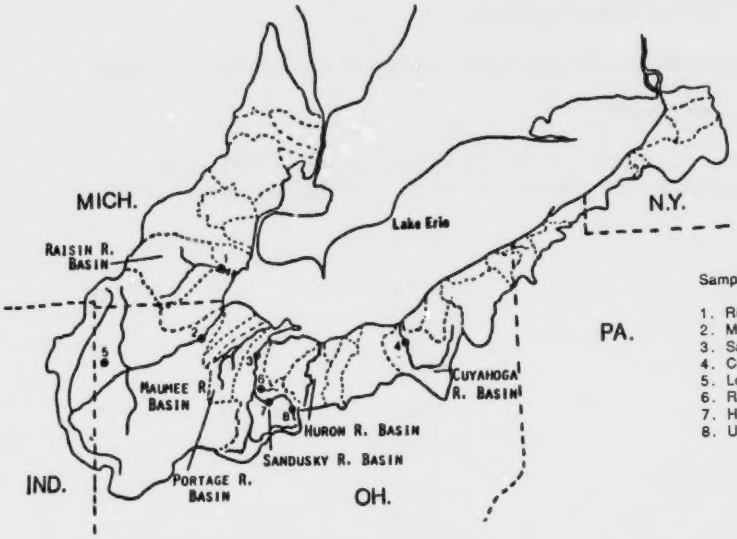
Sampling and Analytical Methods and Calculational Procedures

The sampling methods, analytical procedures and calculational methods are described in the accompanying main report. They have also been described in more detail in the following report.

> Baker, D.B. 1984. Fluvial Transport and Processing of Sediment and Nutrients in Large Agricultural River Basins. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia. EPA-600/3-83-054. January 1984.

Sampling Locations

Locations of Lake Erie Tributary monitoring stations operated by the Water Quality Laboratory at Heidelberg College for the 1982-1985 water years are shown below:



Sampling Locations:

1. River Raisin near Monroe, MI
2. Maumee R. at Bowling Green, OH water intake
3. Sandusky R. near Fremont, OH
4. Cuyahoga R. at Independence, OH
5. Lost Cr. tributary near Defiance, OH
6. Rock Cr. at Tiffin, OH
7. Honey Cr. at Melmore, OH
8. Upper Honey Cr. at New Washington, OH

Historical Nutrient and Sediment Data

Sampling programs of the type illustrated in this Appendix were initiated by the Water Quality Laboratory in 1974. The following table lists the stations and years for which nutrient and sediment data are available.

Transport Stations	U.S. Geological Survey Station Number	Drainage Area Km^2	Mean Annual Discharge Years of Record	m^3/s	cm	Chemical Sampling Period	Number of Samples Analyzed
Sandusky River Stations							
1. Fremont	04198000	3,240	57	27.75	27.0	1974-85	5092[b]
2. Mexico	04197000	2,005	55	16.62	26.2	1974-81	2178
3. Upper Sandusky	04196500	722	57	6.967	28.5	1974-81	2973
4. Bucyrus	04196000	230	40	2.461	33.8	1974-81	2998
Sandusky River Tributaries							
5. Wolf Creek, East	04192450	213	5	1.82	27.0	1976-81	2425
6. Wolf Creek, West	04197300	171.5	5	1.34	24.6	1976-81	2419
7. Honey Cr., Melmore	04197100	386	7	3.908	32.0	1976-85	5075[b]
8. Honey Cr., New Wash	04197020	44.0	3.908	(0.445)[a]	(32.0)[a]	1979-81; 1983-85	2701
9. Tymochtee Creek	04196800	593	19	4.956	26.3	1974-81	2471
10. Broken Sword Cr.	04196200	217	5	2.45	35.5	1976-81	2512
11. Rock Creek	04197170	88.0	3	---	---	1983-85	1496[b]
Other Lake Erie Tributaries							
12. Maumee River	04193500	16,395	58	139.5	26.8	1975-80; 1982-85	3608[b]
13. Raisin	04176500	2,699	43	19.85	23.2	1982-85	1115[b]
14. Cuyahoga	04208000	1,831	52	23.14	39.8	1981-85	1882[b]
15. Portage	04195500	1,109	51	9.091	25.9	1974-78	1856
16. Huron	04199000	961	31	8.496	27.9	1974-79	2027
17. Lost Creek	04185440	11.3	4	---	---	1982-85	2158[b]

[a] Extrapolated from Honey Creek at Melmore.

[b] Sampling continued for the 1986 water year.

List of Tables

The following tables for the indicated stations and water years include:

1. USGS discharge for each month and the entire water year.
2. The ratios of the monthly USGS discharge to the discharge observed in the monitoring program.
3. The number of samples analyzed each month.
4. The monthly and water year loads of suspended solids (SS), total phosphorus (TP), soluble reactive phosphorus (SRP), nitrate plus nitrite-nitrogen (NO23-N), total Kjeldahl nitrogen (TKN), and Chloride (Cl).

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The following figures for the indicated stations and water years include annual hydrographs, sedigraphs and chemographs for total phosphorus, soluble reactive phosphorus, nitrate plus nitrite-nitrogen, and conductivity.

Figure	Station	Water Year	Page
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2	Maumee	1983	118
3	Maumee	1984	120
4	Maumee	1985	122
5	Sandusky	1982	124
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9	Cuyahoga	1982	132
10	Cuyahoga	1983	134
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12	Cuyahoga	1985	138
13	Raisin	1982	140
14	Raisin	1983	142
15	Raisin	1984	144
16	Raisin	1985	146
17	Honey Creek	1982	148
18	Honey Creek	1983	150
19	Honey Creek	1984	152
20	Honey Creek	1985	154
21	Rock Creek	1983	156
22	Rock Creek	1984	158
23	Rock Creek	1985	160
24	Upper Honey Creek	1983	162
25	Upper Honey Creek	1984	164
26	Upper Honey Creek	1985	166
27	Lost Creek	1982	168
28	Lost Creek	1983	169
29	Lost Creek	1984	170
30	Lost Creek	1985	171

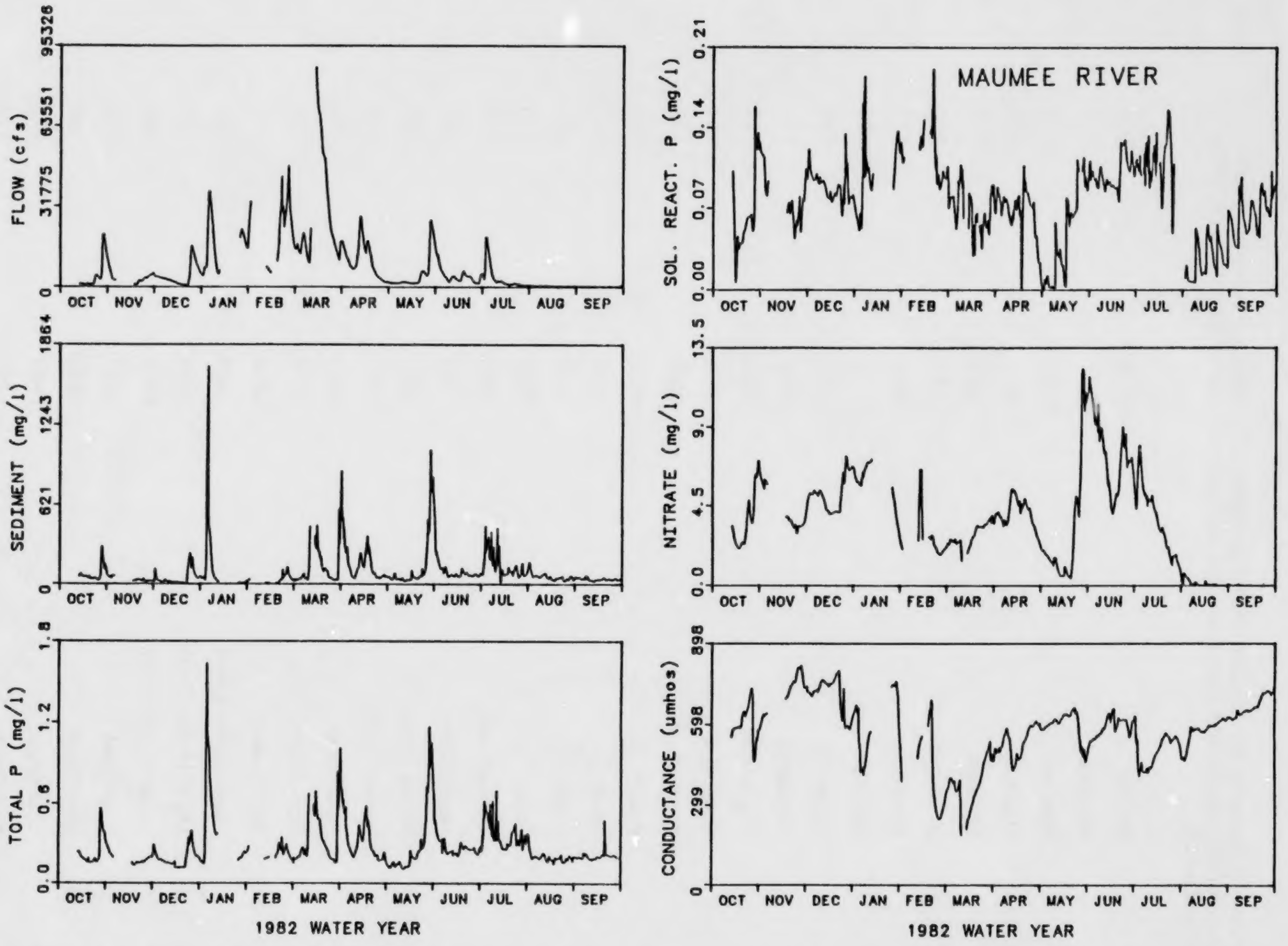

Figure 1. Annual hydrograph, sedigraph and nutrient chemograph for the Maumee River (USGS No. 01493500) during the 1982 water year.

Table 1. Monthly loads and discharge for the Maumee River for water year 1982. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	312.67	1.371	33	41485	116.4	33.16	1728	523.6	8723.4
Nov	207.92	1.387	21	7127	42.0	17.11	878	242.9	8860.8
Dec	329.96	1.043	39	29714	83.3	29.46	1948	382.4	13425.9
Jan	632.33	0.801	30	162744	360.7	67.53	3289	1027.5	23659.8
Feb	872.23	0.964	29	47908	223.7	97.07	2006	1213.2	23109.4
Mar	2898.23	1.403	54	519923	1153.5	182.75	7769	4825.6	42624.7
Apr	807.53	1.008	58	191453	346.7	55.84	3563	1437.9	17554.9
May	380.83	1.040	46	165879	239.7	29.19	2824	868.2	11557.4
Jun	341.43	1.053	37	51629	117.6	33.40	2828	458.1	10159.3
Jul	269.69	1.108	60	61042	121.7	28.50	1523	454.2	5444.4
Aug	31.21	1.212	36	2005	6.6	0.82	4	43.7	1285.4
Sep	23.43	1.511	36	962	5.0	1.60	<1	25.9	1405.4
Totals	7107.47		479	1281870	2816.9	576.42	28361	11503.0	167811.0

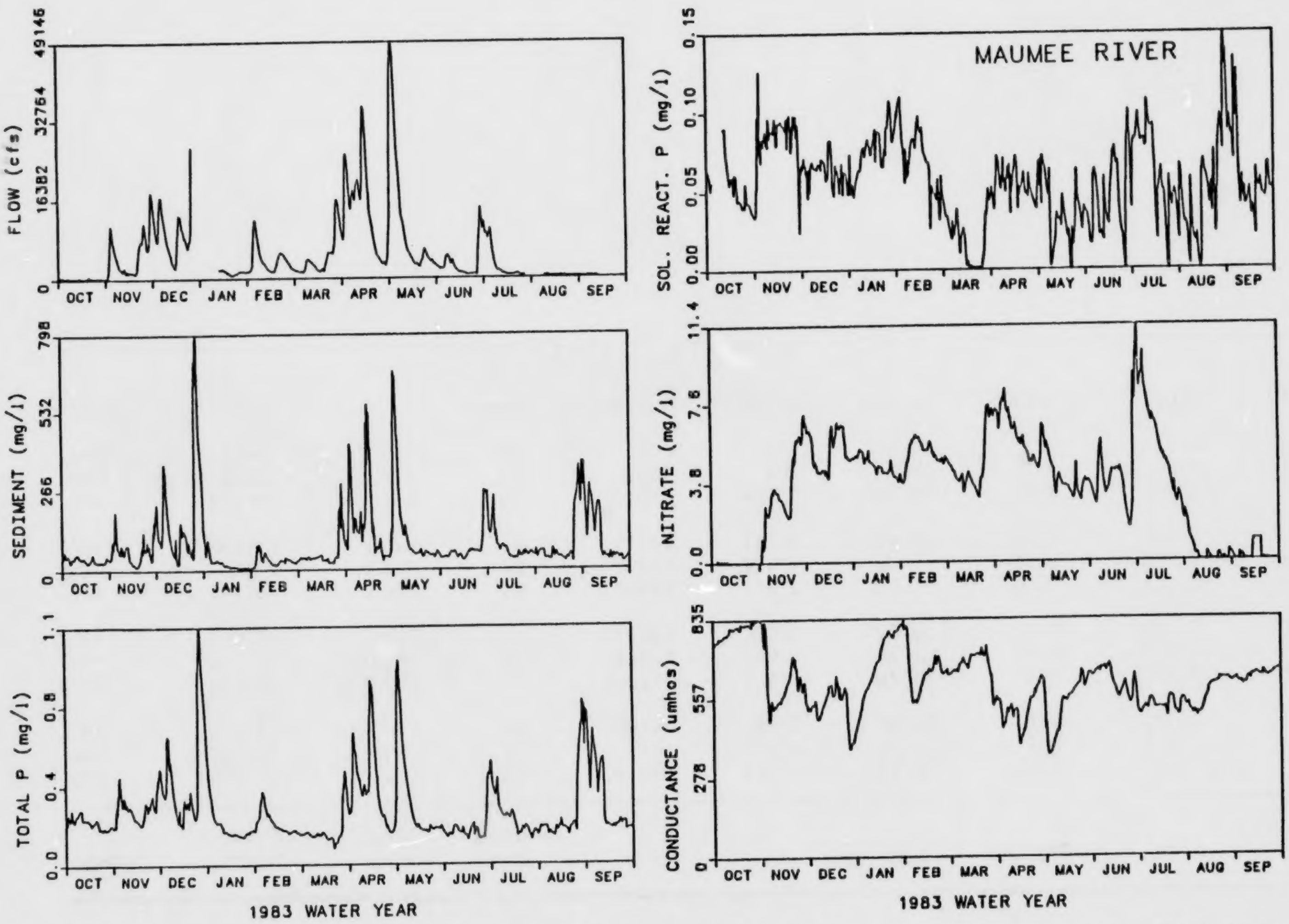

Figure 2. Annual hydrograph, sedigraph and nutrient chemograph for the Maumee River (USGS No. 01493500) during the 1983 water year.

Table 2. Monthly loads and discharge for the Maumee River for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	23.19	1.617	35	950	5.0	1.28	<1	25.9	1820.6
Nov	384.74	1.042	88	34635	123.0	32.31	1723	589.7	16508.2
Dec	976.38	1.024	55	278021	562.7	61.61	5266	2311.9	25741.6
Jan	224.68	1.044	38	9174	54.1	15.65	1102	309.0	7378.4
Feb	291.81	1.048	35	13220	67.7	20.96	1528	351.6	11557.5
Mar	336.54	1.045	44	32941	80.1	8.27	1893	442.3	12470.7
Apr	1069.93	1.021	63	243090	517.7	62.83	6971	2162.6	22632.2
May	959.05	1.065	45	274559	531.6	49.86	4769	2041.8	18416.8
Jun	209.68	1.026	34	25045	53.1	13.17	1088	316.4	6797.0
Jul	217.50	1.120	36	30689	71.7	17.00	1861	363.9	4888.5
Aug	37.47	1.263	38	2570	8.0	1.63	29	49.2	1610.7
Sep	17.34	1.310	35	1756	5.2	1.11	3	21.9	1017.4
Totals	4748.30		546	946649	2079.9	285.70	26233	8986.0	130840.0

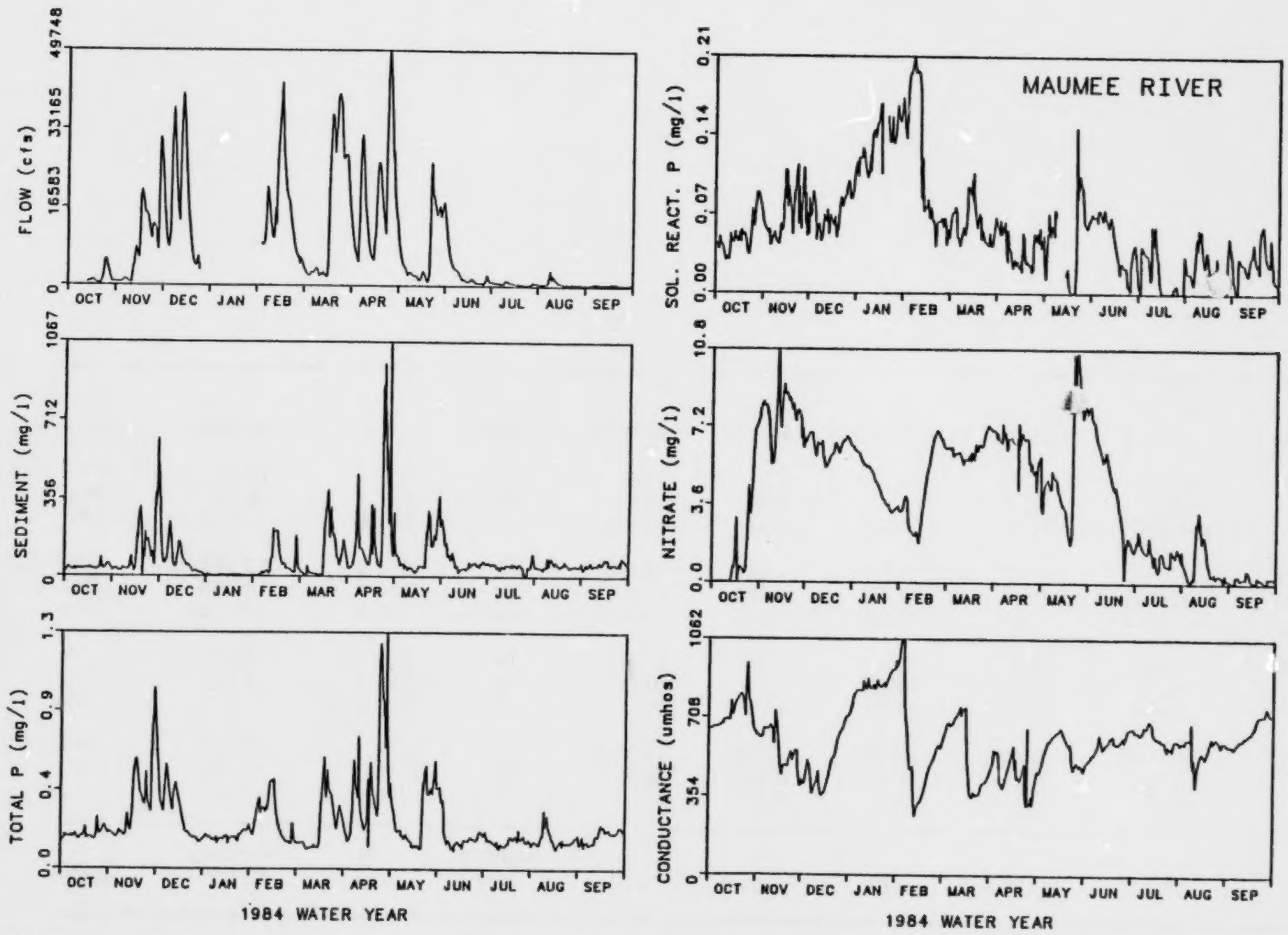

Figure 3. Annual hydrograph, sedigraph and nutrient chemograph for the Maumee River (USGS No. 01493500) during the 1984 water year.

Table 3. Monthly loads and discharge for the Maumee River for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	84.41	1.058	36	3786	18.0	5.42	273	101.8	5401.7
Nov	616.69	0.909	53	137804	343.0	48.26	4837	1386.9	17371.3
Dec	1012.32	0.904	37	128897	448.3	66.96	6118	1806.6	20496.0
Jan	76.03	1.015	35	286	15.0	10.93	335	104.0	4350.3
Feb	789.77	0.822	34	60073	251.5	86.68	3374	1504.4	26552.7
Mar	1136.95	1.038	40	183798	427.8	64.15	7336	1935.6	22843.8
Apr	1308.90	0.939	66	432218	848.7	53.89	7874	2850.1	24007.1
May	541.69	0.908	37	103840	232.4	38.88	4160	863.7	13064.8
Jun	165.07	1.023	34	17607	43.4	9.90	982	189.6	4412.6
Jul	55.20	1.446	36	2741	8.8	1.14	76	59.1	2820.9
Aug	59.00	1.342	40	3328	12.2	2.06	78	76.1	3168.3
Sep	32.55	1.711	34	1930	6.5	0.95	7	42.4	2021.0
Totals	5878.54		482	1076310	2655.5	389.22	35449	10920.1	146510.0

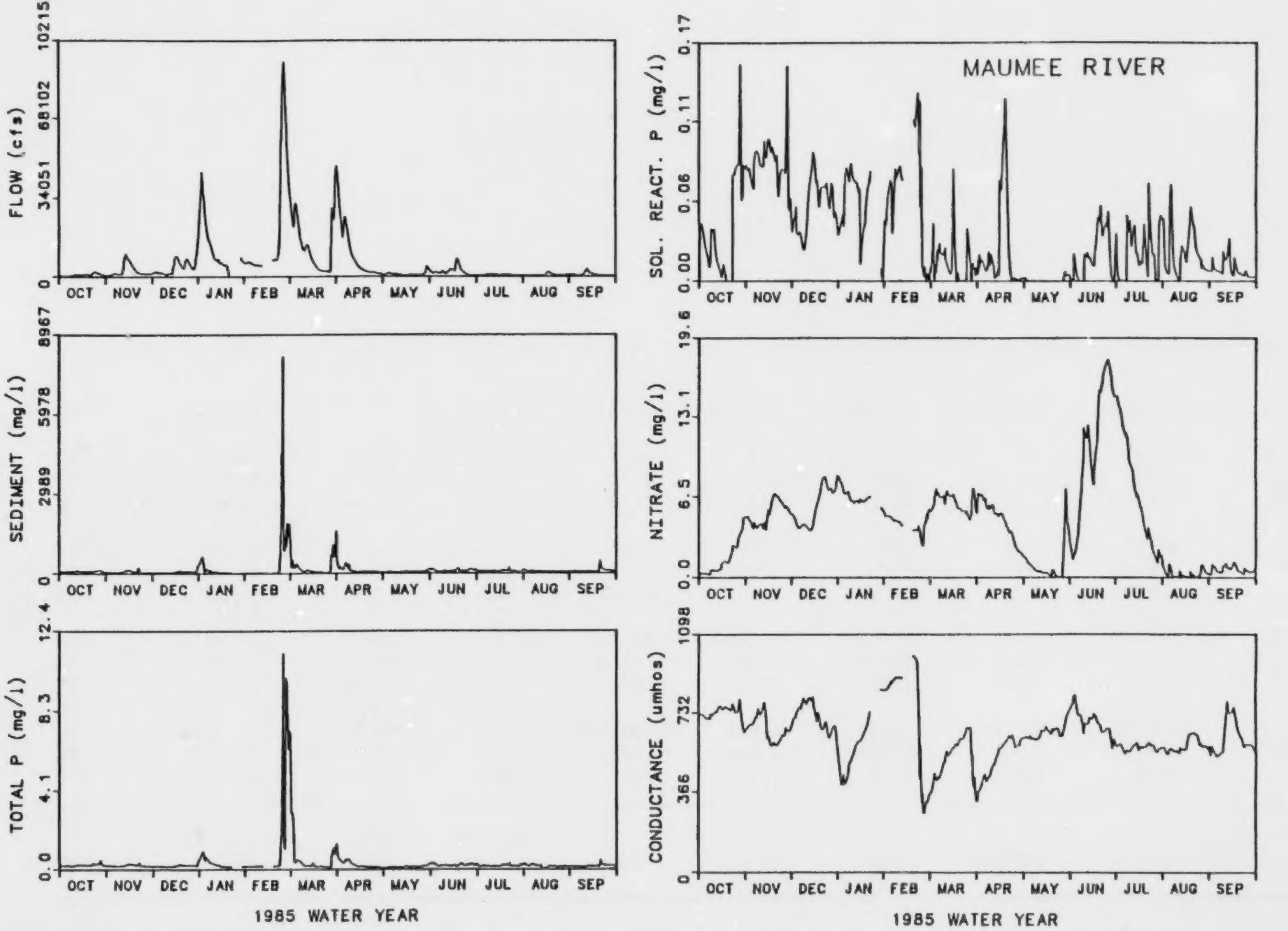

Figure 4. Annual hydrograph, sedigraph and nutrient chemograph for the Maumee River (USGS No. 01493500) during the 1985 water year.

Table 4. Monthly loads and discharge for the Maumee River for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	80.04	1.302	36	6802	22.4	---	151	103.1	4646.1
Nov	183.49	1.065	34	13460	46.3	---	957	253.5	8468.2
Dec	307.00	0.946	34	29498	81.6	---	2054	391.1	13586.7
Jan	564.38	0.847	31	103556	280.7	---	3746	1159.7	15164.1
Feb	990.55	0.843	42	245853	498.7	---	3892	1613.6	26412.3
Mar	1027.50	0.946	54	185258	440.0	---	6438	1798.1	23304.2
Apr	788.55	0.936	49	278980	445.2	---	4644	1684.5	14551.8
May	94.28	1.200	37	6323	16.3	---	190	112.0	4798.3
Jun	156.85	1.011	33	16174	36.5	---	1579	209.4	7226.7
Jul	55.51	1.494	35	4330	9.8	---	405	79.4	2473.2
Aug	51.35	1.418	35	2480	7.6	---	11	70.7	3016.5
Sep	66.48	1.385	35	4347	10.8	---	49	86.6	4012.5
Totals	4365.94		455	897064	1895.8	---	24116	7561.6	127661.0

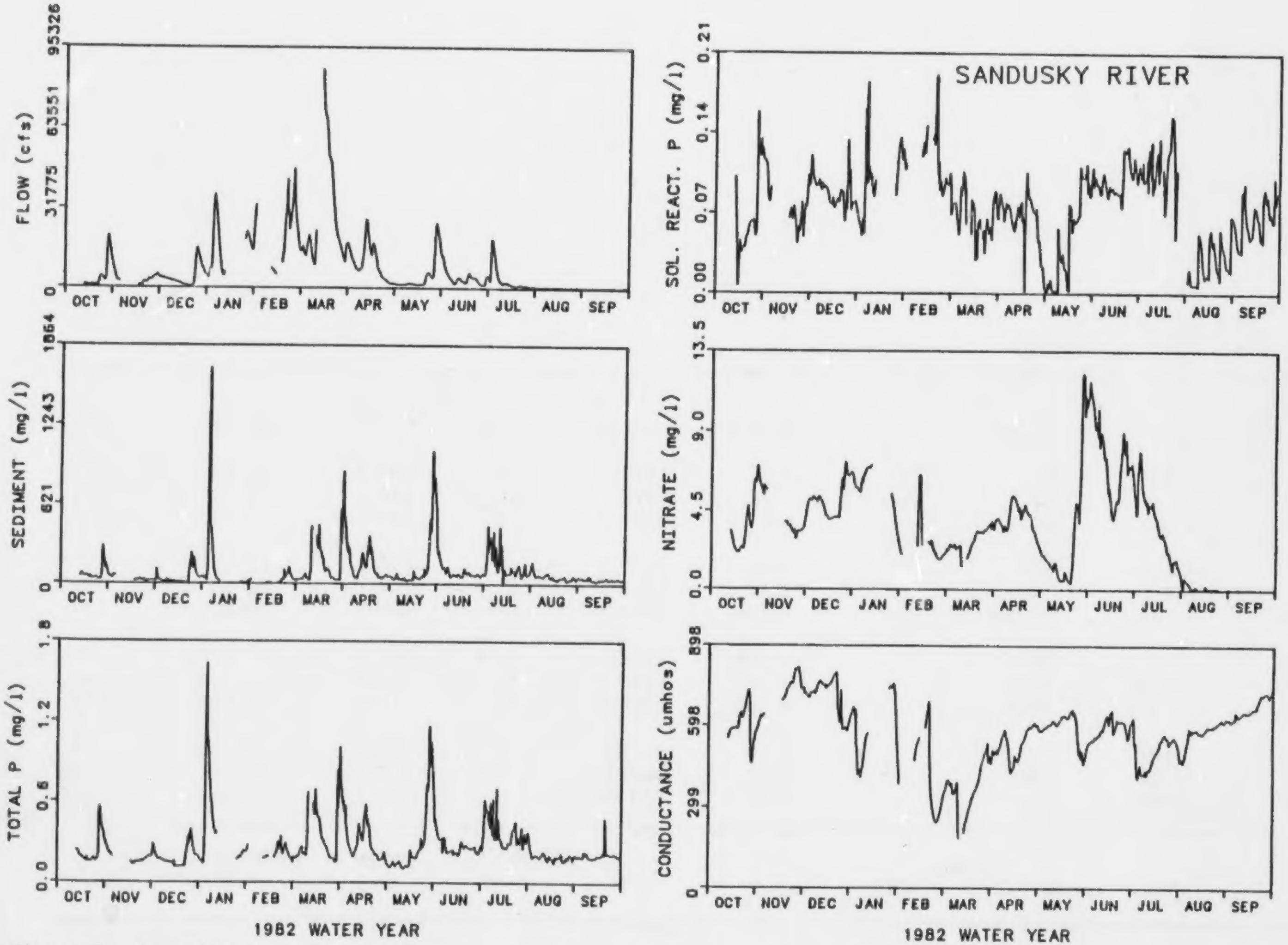

Figure 5. Annual hydrograph, sedigraph and nutrient chemograph for the Sandusky River (USGS No. 04198000) during the 1982 water year.

Table 5. Monthly loads and discharge for the Sandusky River for water year 1982. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	40.22	1.008	36	1592	6.4	2.77	127	40.9	1149.2
Nov	45.25	1.000	35	933	5.8	2.20	132	40.7	1797.1
Dec	130.95	1.072	35	12084	33.7	10.09	544	138.9	4232.4
Jan	171.34	1.850	28	7615	45.5	16.48	519	201.2	4415.9
Feb	235.33	1.043	39	17626	59.8	20.48	388	293.6	3587.7
Mar	408.89	1.020	63	170720	241.4	18.57	1132	932.2	6833.6
Apr	158.13	1.651	37	74595	110.8	6.77	526	404.4	3468.7
May	80.44	1.137	35	83410	91.9	5.57	747	319.7	1745.3
Jun	49.70	1.133	45	10012	16.6	3.69	484	69.1	1571.0
Jul	62.49	1.053	46	14657	26.2	3.16	391	110.6	1311.2
Aug	3.98	1.042	34	142	0.5	0.09	<1	3.7	195.6
Sep	3.52	1.012	36	89	0.4	0.07	<1	3.0	213.6
Totals	1390.24		469	393473	639.0	89.95	4990	2557.9	30521.1

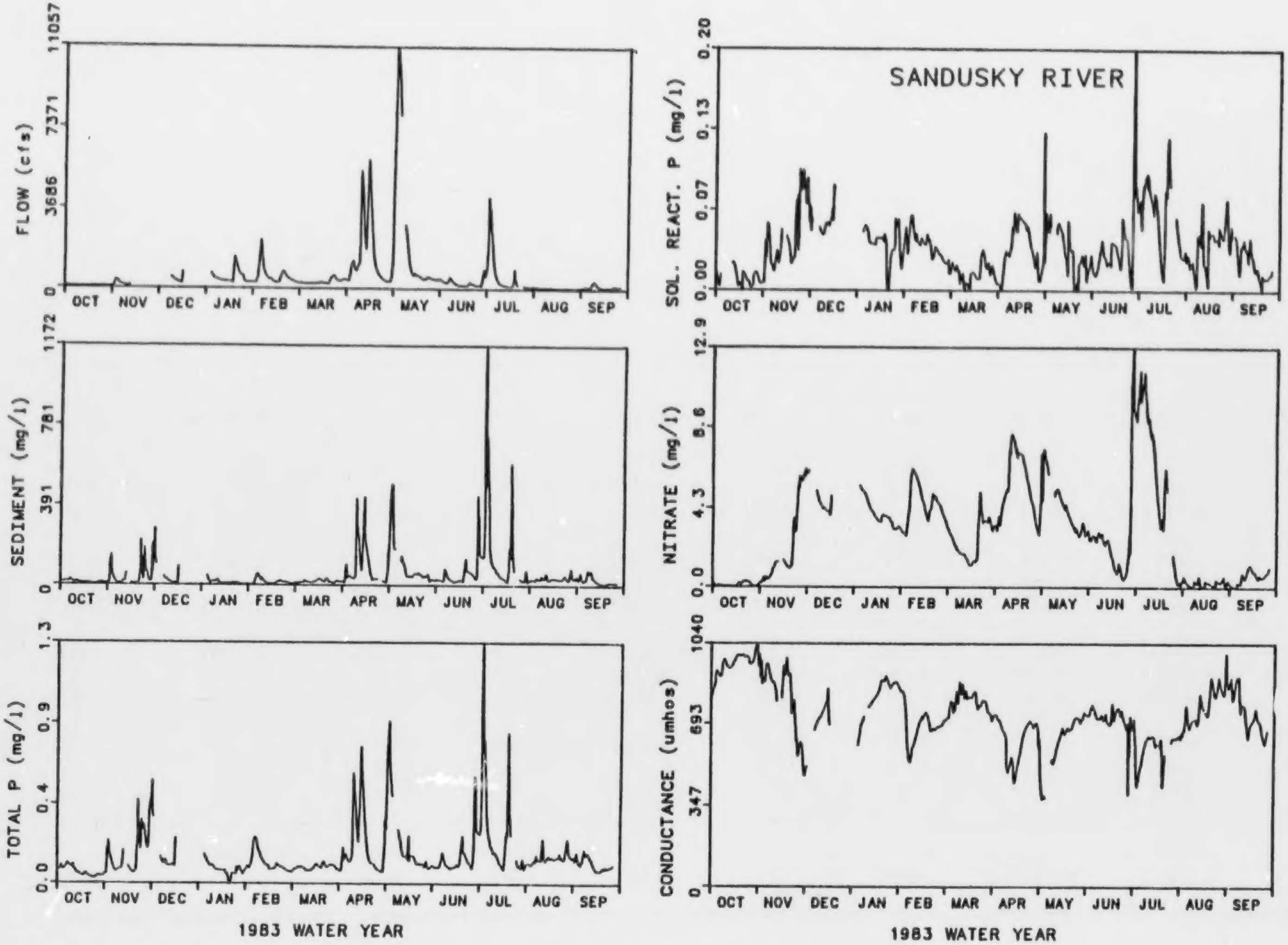

Figure 6. Annual hydrograph, sedigraph and nutrient chemograph for the Sandusky River (USGS No. 04198000) during the 1983 water year.

Table 6. Monthly loads and discharge for the Sandusky River for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	3.41	0.976	35	38	0.2	0.03	<1	2.1	192.1
Nov	48.97	1.021	63	4595	14.9	3.55	239	62.0	1845.9
Dec	145.76	5.000	21	19824	51.1	11.08	772	217.3	4963.4
Jan	30.93	0.993	28	330	2.1	1.08	125	17.6	1289.2
Feb	40.56	1.029	32	996	5.8	1.69	192	32.2	1526.2
Mar	24.45	1.061	35	423	2.2	0.39	69	17.6	1170.0
Apr	113.60	1.165	40	19611	41.1	5.33	746	188.8	3052.5
May	166.96	1.142	44	40587	82.4	8.15	996	327.5	3549.7
Jun	19.09	0.915	38	1372	3.1	0.78	74	18.9	707.6
Jul	43.29	1.062	45	18562	24.9	3.22	402	94.3	935.6
Aug	3.90	1.164	36	137	0.5	0.14	1	3.1	199.8
Sep	8.68	1.212	29	311	1.1	0.22	5	7.0	370.0
Totals	649.60		446	106787	235.4	35.66	3621	988.5	19802.0

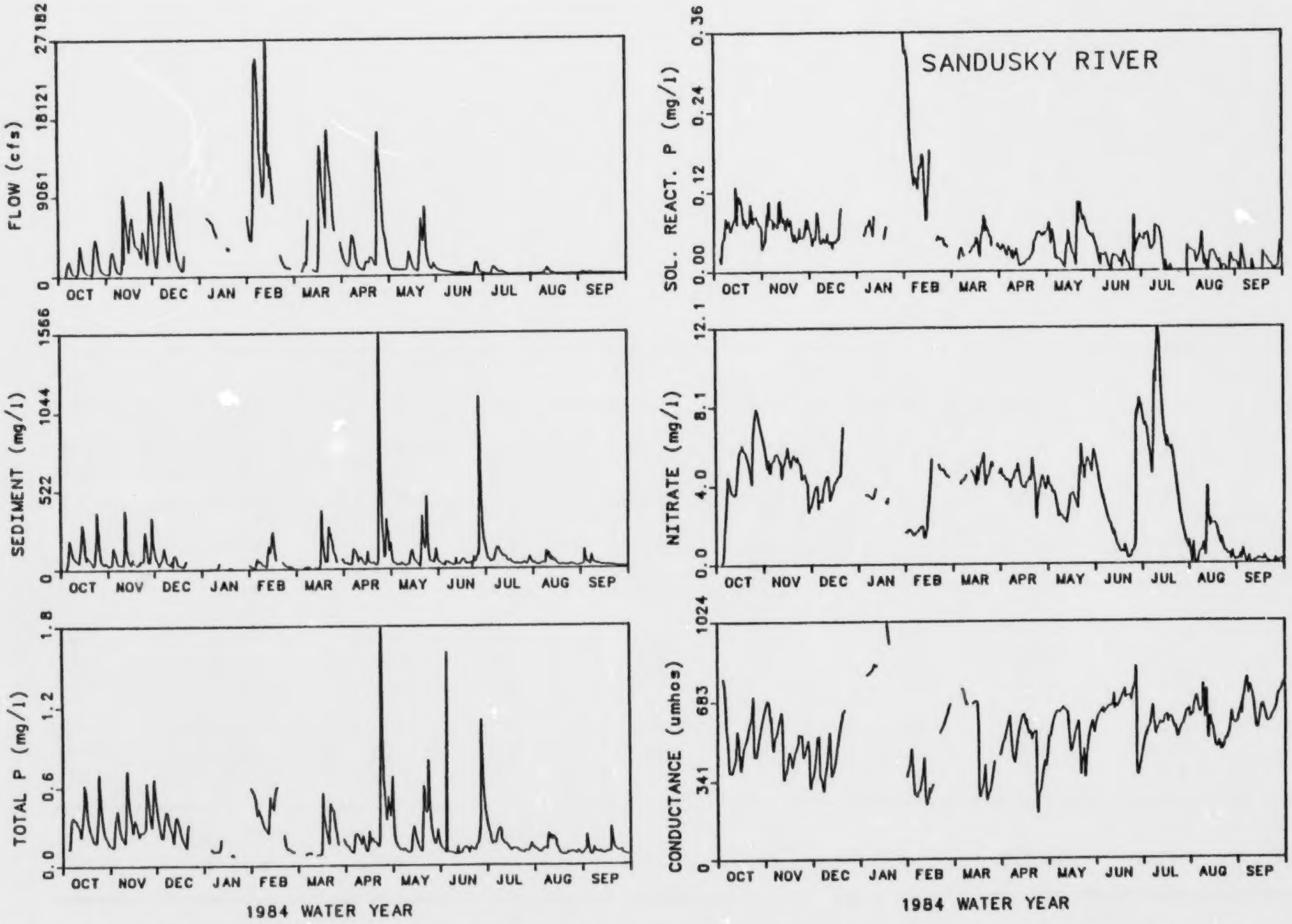

Figure 7. Annual hydrograph, sedigraph and nutrient chemograph for the Sandusky River (USGS No. 04198000) during the 1984 water year.

Table 7. Monthly loads and discharge for the Sandusky River for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	75.10	0.991	41	12952	31.8	6.27	412	127.3	1798.6
Nov	254.35	0.981	49	31375	107.5	18.31	1191	403.5	5487.6
Dec	220.37	1.101	24	15570	71.9	12.11	823	252.4	4077.5
Jan	76.32	0.500	14	7319	29.4	7.20	337	78.3	2942.8
Feb	532.52	0.951	32	40443	214.2	80.30	1125	1019.9	9444.9
Mar	356.06	1.119	34	54651	114.8	18.39	1663	470.5	5873.4
Apr	243.73	1.008	39	91369	145.8	10.32	947	512.8	3671.7
May	118.19	0.977	40	19018	43.5	7.76	520	160.6	2507.4
Jun	25.59	0.941	45	4796	8.1	0.73	91	33.3	739.7
Jul	17.99	1.066	36	1529	3.5	0.63	122	20.8	579.1
Aug	12.08	1.082	51	642	1.9	0.24	16	11.1	453.0
Sep	8.18	1.129	37	279	0.9	0.06	2	8.0	351.0
Totals	1940.47		442	279943	773.3	162.31	7251	3102.0	37926.6

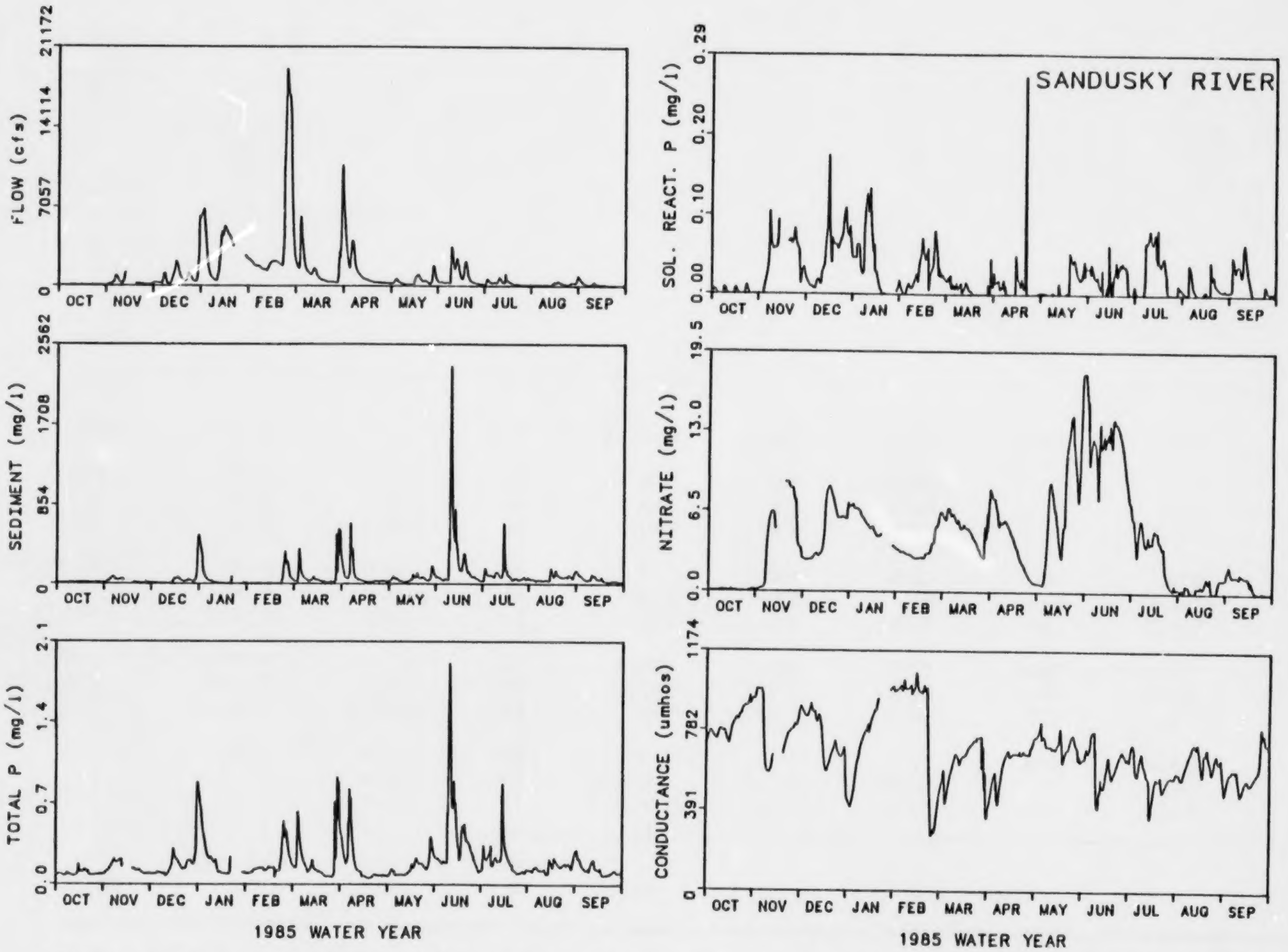

Figure 8. Annual hydrograph, sedigraph and nutrient chemograph for the Sandusky River (USGS No. 04198000) during the 1985 water year.

Table 8. Monthly loads and discharge for the Sandusky River for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	4.78	1.200	36	58	0.4	---	<1	3.8	222.5
Nov	24.62	1.446	25	1010	4.3	---	110	24.3	1024.8
Dec	74.80	1.083	33	12582	27.8	---	466	110.7	3104.6
Jan	81.54	0.471	28	7826	24.0	---	360	83.7	3210.4
Feb	206.66	0.693	40	28350	64.8	---	880	290.6	6757.6
Mar	118.08	1.063	49	20658	41.3	---	681	169.9	3508.8
Apr	114.20	0.965	44	23880	46.1	---	722	191.6	2854.2
May	37.05	1.036	38	3112	7.4	---	313	42.1	1538.1
Jun	63.00	1.018	61	34194	43.4	---	779	143.8	1758.3
Jul	20.86	1.022	40	3003	5.8	---	86	27.4	659.5
Aug	13.89	1.015	35	1300	2.6	---	10	14.3	534.2
Sep	10.29	1.184	35	794	2.0	---	14	10.1	333.7
Totals	769.78		464	136767	269.9	---	4422	1112.2	25506.6

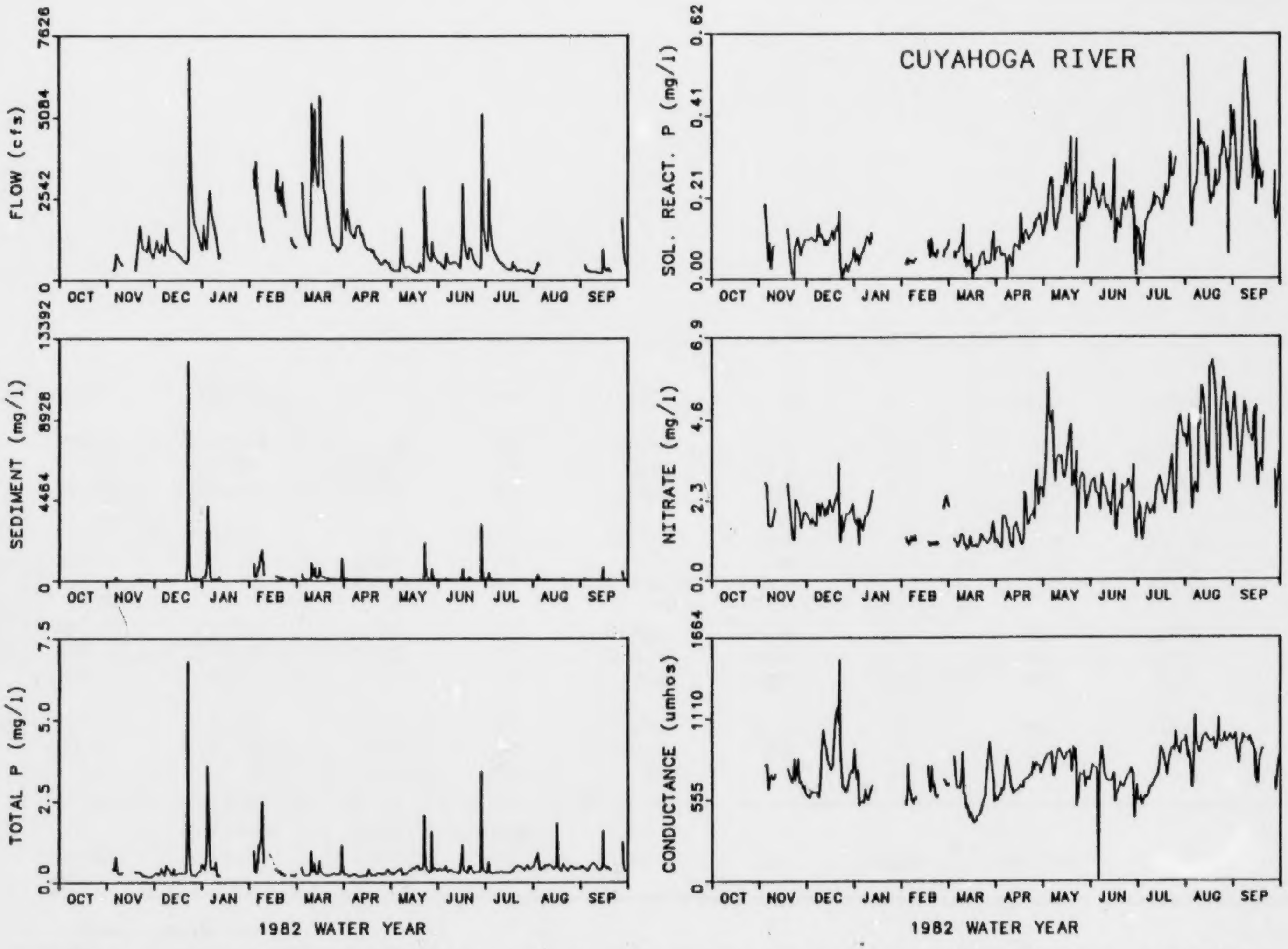

Figure 9. Annual hydrograph, sedigraph and nutrient chemograph for the Cuyahoga River (USGS No. 04208000) during the 1982 water year.

Table 9. Monthly loads and discharge for the Cuyahoga River for water year 1982. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	45.26	----	0	3168	22.6	14.03	158	58.8	4278.2
Nov	57.58	1.660	21	2488	16.1	3.75	101	69.7	5460.2
Dec	102.84	1.103	37	28830	51.3	6.72	194	135.8	11566.1
Jan	106.77	2.562	17	50266	77.5	8.48	190	128.3	8935.1
Feb	144.96	1.443	58	56619	81.7	8.65	175	265.6	15002.9
Mar	173.36	1.072	64	48749	64.7	8.60	196	296.3	14836.9
Apr	90.91	1.072	36	4704	22.3	7.50	138	117.3	8336.3
May	46.34	1.063	44	11704	26.3	7.71	135	66.1	4903.5
Jun	63.11	1.061	45	18284	38.9	10.69	141	95.9	5194.1
Jul	45.39	0.983	47	4374	17.6	6.82	100	46.5	3913.6
Aug	17.60	4.166	44	2527	11.8	4.92	61	24.5	1795.3
Sep	25.67	1.141	34	3825	16.5	6.97	90	37.0	2570.4
Totals	919.79		447	235538	447.3	94.84	1682	1341.7	86792.6

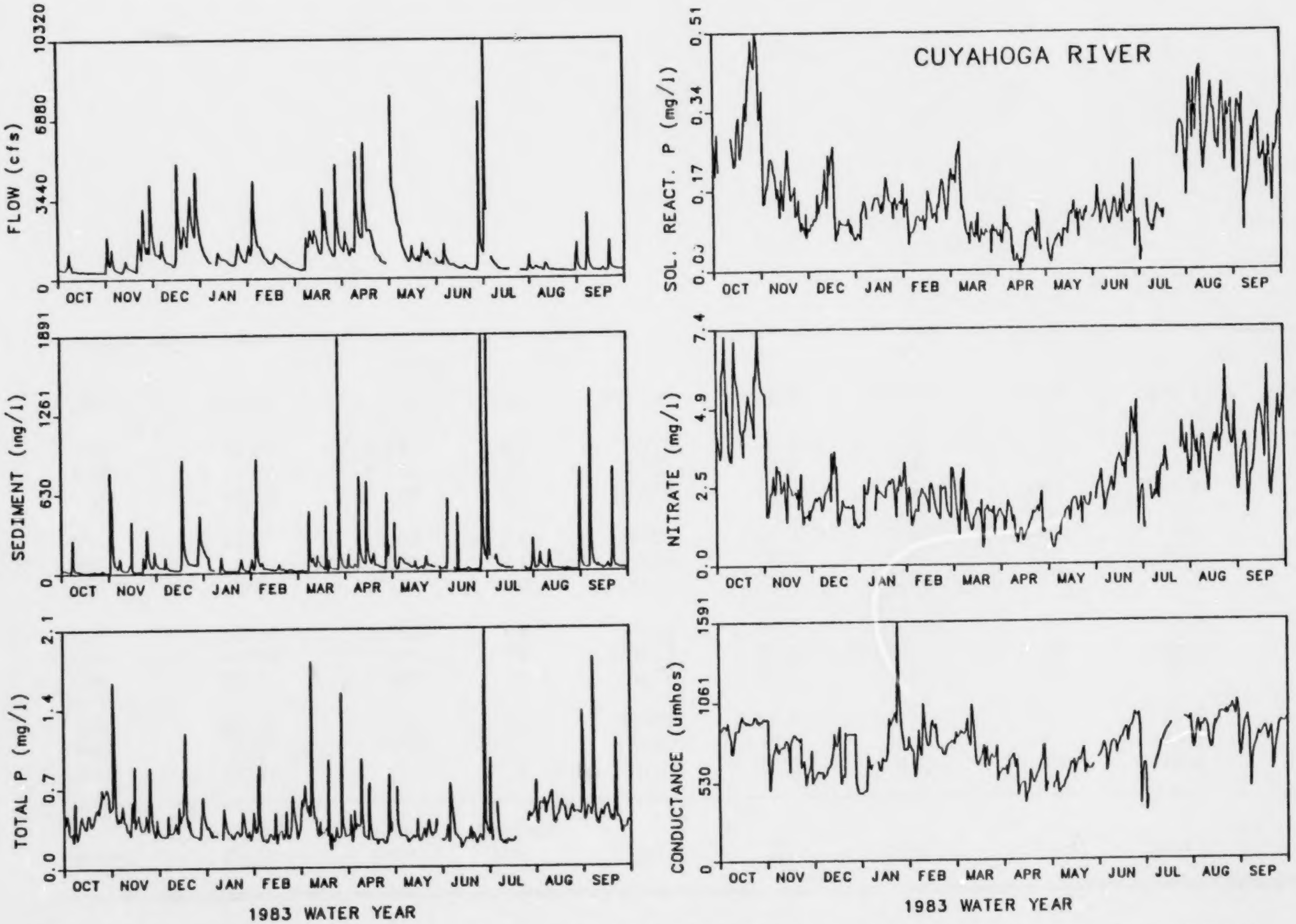

Figure 10. Annual hydrograph, sedigraph and nutrient chemograph for the Cuyahoga River (USGS No. 04208000) during the 1983 water year.

Table 10. Monthly loads and discharge for the Cuyahoga River for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	17.25	0.622	37	466	7.6	5.68	86	26.5	1856.6
Nov	78.21	1.095	62	9709	37.1	11.22	164	108.0	6125.1
Dec	139.03	1.084	49	19418	55.2	16.45	264	128.6	13073.4
Jan	71.16	1.139	34	3604	23.9	9.63	159	58.2	7512.8
Feb	75.80	1.057	37	8625	27.8	8.46	143	83.2	7994.0
Mar	109.87	1.039	50	18585	47.9	10.08	168	163.0	10864.8
Apr	128.04	1.081	53	21756	47.6	6.62	156	157.4	8197.7
May	129.24	1.215	31	13033	45.0	8.99	158	115.1	7953.3
Jun	53.67	1.093	37	22458	29.5	5.90	132	88.4	3904.7
Jul	64.56	1.322	29	36476	31.5	5.26	121	123.8	3424.5
Aug	23.47	0.837	40	2669	13.7	7.28	86	24.9	2510.6
Sep	29.70	0.948	43	7347	19.0	6.84	99	38.6	2845.9
Totals	920.00		502	164145	385.6	102.41	1737	1115.6	76263.4

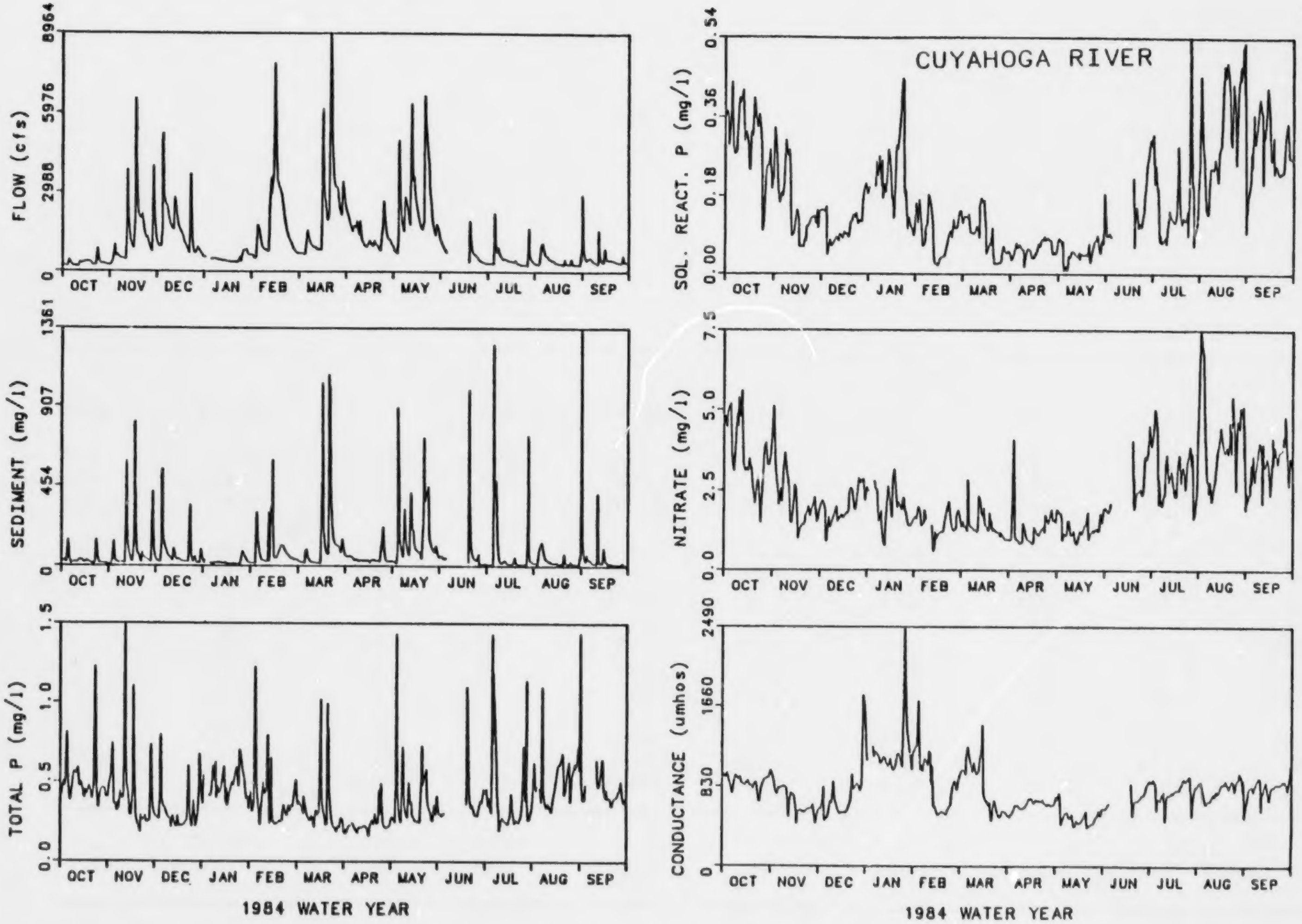

Figure 11. Annual hydrograph, sedigraph and nutrient chemograph for the Cuyahoga River (USGS No. 04208000) during the 1984 water year.

Table 11. Monthly loads and discharge for the Cuyahoga River for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	24.13	1.078	36	952	12.9	7.41	84	23.0	2371.3
Nov	107.72	1.011	41	18929	53.6	12.92	193	138.3	7659.9
Dec	111.89	0.994	35	12762	38.3	11.13	203	119.9	10957.3
Jan	35.57	1.032	33	835	17.3	7.20	67	115.7	7366.5
Feb	139.48	1.263	32	15923	52.6	9.73	188	252.1	18285.4
Mar	169.65	0.988	44	46210	65.8	10.39	221	285.7	18814.7
Apr	104.95	1.037	35	5489	25.1	6.11	140	136.4	8800.6
May	181.77	1.045	37	41885	76.6	9.00	222	214.9	10652.9
Jun	48.07	1.839	21	6641	21.3	6.71	122	51.5	3785.5
Jul	37.13	1.008	42	6662	19.3	5.00	107	43.0	3478.3
Aug	37.58	1.044	42	5431	21.9	10.37	135	42.6	3716.3
Sep	32.06	0.995	37	1406	14.4	9.35	107	32.6	3207.0
Totals	1030.01		435	163123	419.1	105.31	1789	1455.7	99095.7

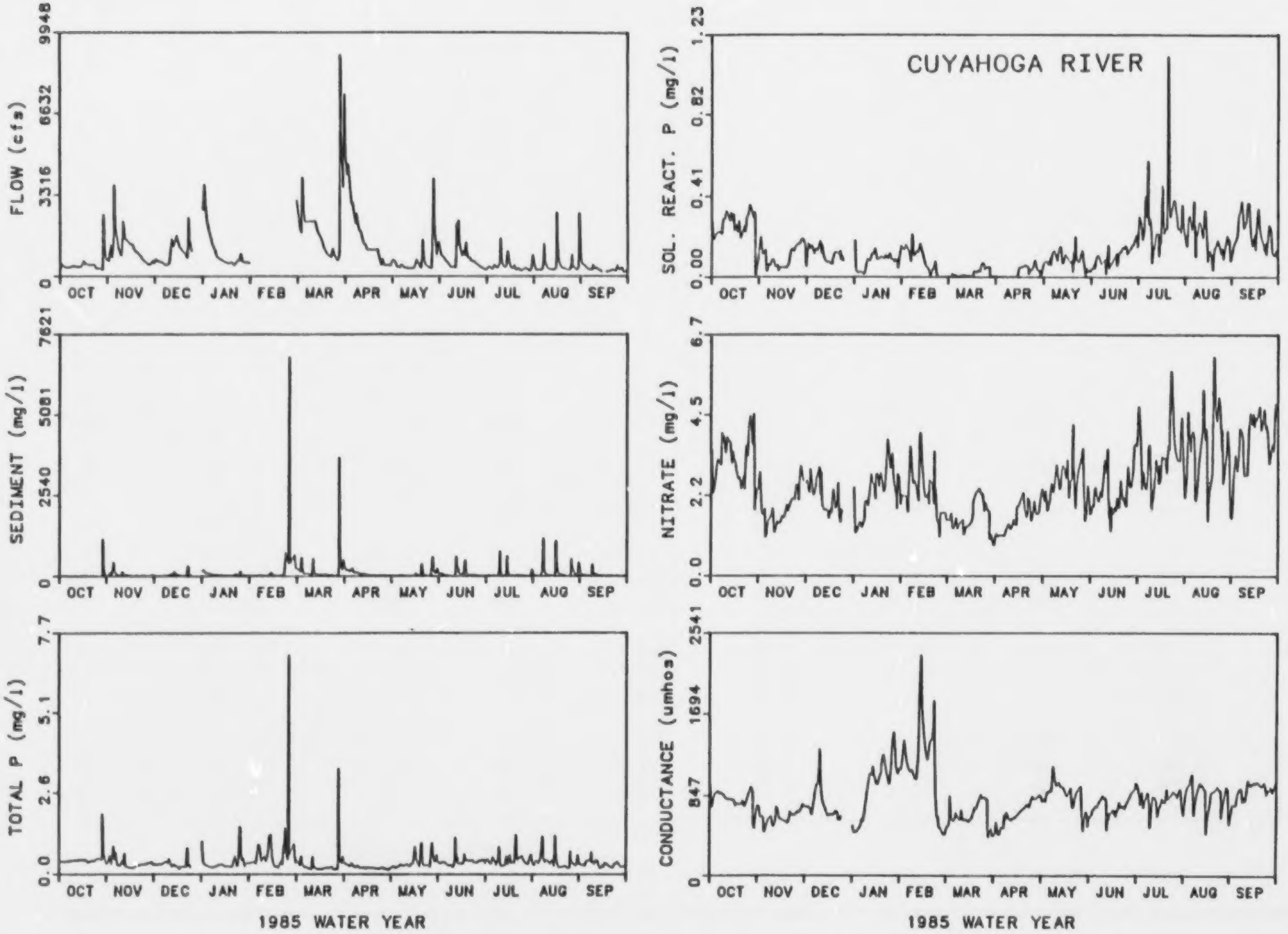

Figure 12. Annual hydrograph, sedigraph and nutrient chemograph for the Cuyahoga River (USGS No. 04208000) during the 1985 water year.

Table 12. Monthly loads and discharge for the Cuyahoga River for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	37.96	0.980	38	3901	20.9	---	116	44.9	3433.5
Nov	84.91	1.054	36	6711	33.2	---	149	97.1	6119.0
Dec	95.80	1.495	32	7005	37.3	---	203	286.6	8938.1
Jan	73.73	1.012	34	5338	25.2	---	150	77.0	10624.1
Feb	132.76	1.104	43	113541	166.2	---	258	283.7	24814.2
Mar	171.70	1.071	51	63134	76.3	---	248	278.8	14432.3
Apr	126.07	1.001	34	19666	34.8	---	169	126.5	9622.7
May	51.14	1.030	42	8228	26.0	---	121	65.3	5391.4
Jun	55.51	1.034	45	5816	23.5	---	123	55.7	4944.9
Jul	33.08	0.998	42	3524	16.0	---	104	66.5	3301.9
Aug	37.64	1.068	43	10050	19.4	---	111	69.9	3639.0
Sep	21.41	1.044	35	710	7.0	---	78	20.2	2312.0
Totals	921.70		475	247625	485.7	---	1830	1472.3	97573.0

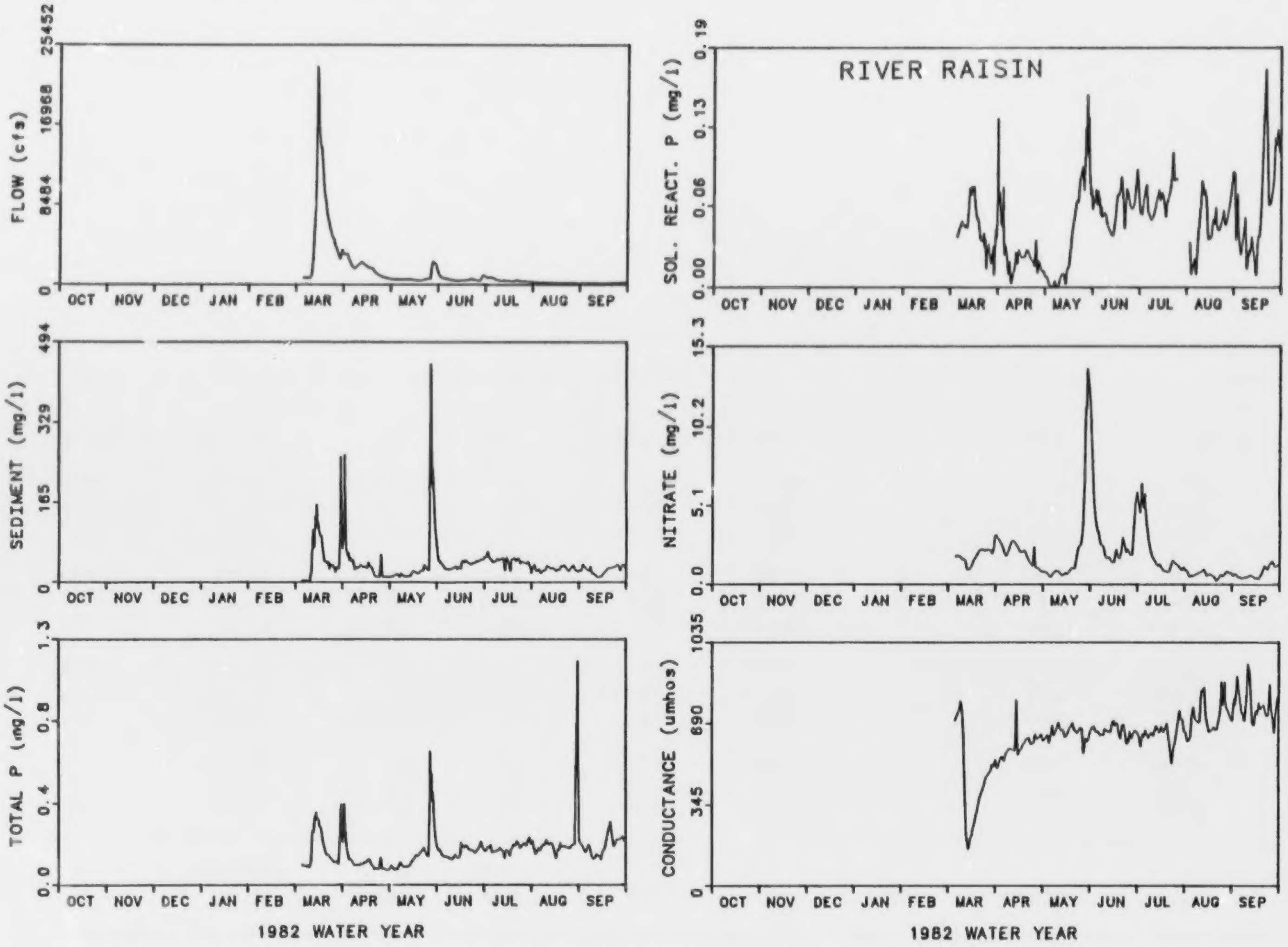

Figure 13. Annual hydrograph, sedigraph and nutrient chemograph for the River Raisin (USGS No. 04176600) during the 1982 water year.

Table 13. Monthly loads and discharge for the River Raisin for water year 1982. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	127.27	---	0	---	---	---	---	---	---
Nov	65.30	---	0	---	---	---	---	---	---
Dec	42.51	---	0	---	---	---	---	---	---
Jan	42.24	---	0	---	---	---	---	---	---
Feb	31.88	---	0	---	---	---	---	---	---
Mar	336.81	0.853	41	28662	86.4	18.84	547	428.0	4737.9
Apr	127.00	0.961	35	6330	18.5	4.19	299	116.8	3500.4
May	55.99	1.074	32	6296	15.0	3.56	311	82.1	1949.0
Jun	41.51	1.084	35	1673	7.3	2.74	155	35.3	1483.6
Jul	31.85	1.049	27	1470	6.0	2.23	100	25.2	1107.9
Aug	12.18	1.061	27	332	2.7	0.59	8	10.5	571.2
Sep	10.73	1.177	26	285	2.2	0.75	9	10.2	597.0
Totals	925.26		223	45047	138.2	32.89	1428	708.0	13946.9

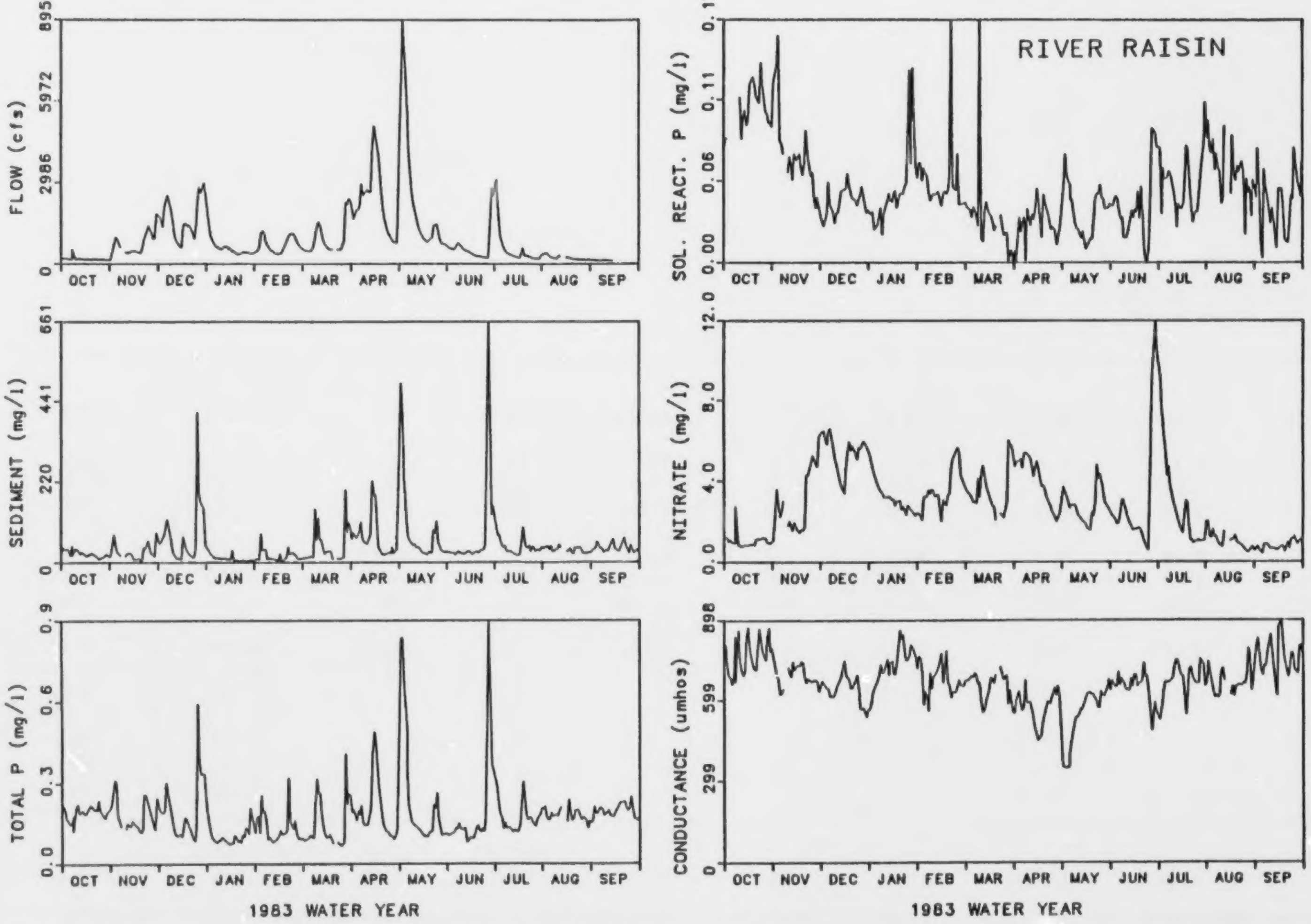

Figure 14. Annual hydrograph, sedigraph and nutrient chemograph for the River Raisin (USGS No. 04176600) during the 1983 water year.

Table 14. Monthly loads and discharge for the River Raisin for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	13.42	1.138	27	331	2.5	1.32	16	8.1	615.0
Nov	60.42	1.381	24	2144	11.6	4.26	222	58.0	2546.2
Dec	132.68	1.210	27	12098	31.1	5.39	743	177.0	5044.4
Jan	46.84	1.317	27	600	5.0	2.19	158	38.0	1857.8
Feb	53.06	1.245	24	1195	8.0	3.14	203	54.3	2052.8
Mar	72.84	1.159	27	5281	14.7	1.99	308	82.0	2485.7
Apr	173.86	1.235	26	15399	42.7	5.23	755	216.0	4487.4
May	184.69	1.310	26	34169	80.1	8.53	565	315.4	3552.4
Jun	52.87	1.372	26	3954	11.2	2.63	274	59.9	1610.5
Jul	52.69	1.524	26	3240	11.0	3.07	284	64.4	1470.9
Aug	20.72	1.407	27	742	3.8	1.39	23	18.6	815.2
Sep	10.35	1.229	25	393	2.0	0.45	8	9.3	536.5
Totals	874.44		312	79547	223.8	39.59	3560	1101.0	27074.8

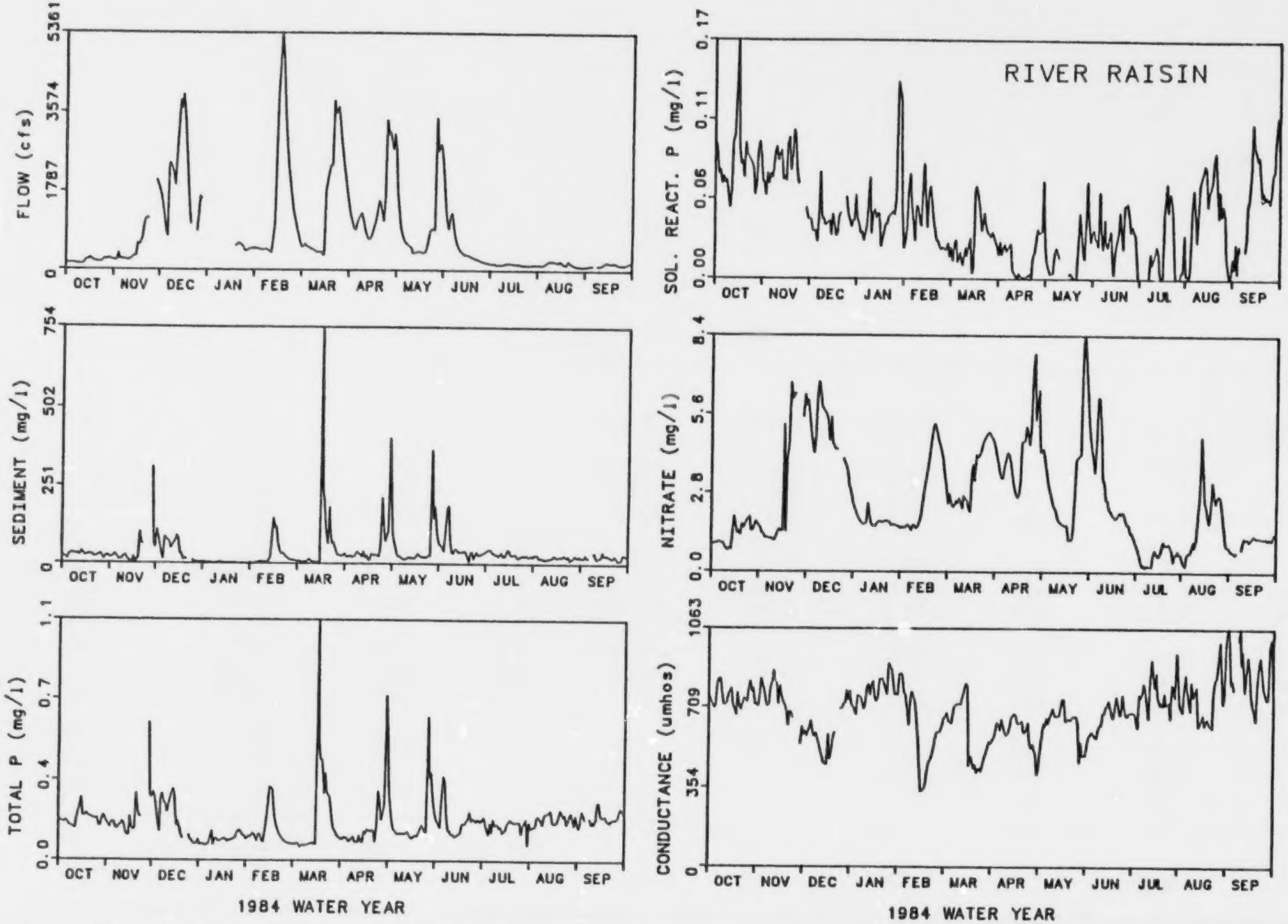

Figure 15. Annual hydrograph, sedigraph and nutrient chemograph for the River Raisin (USGS No. 04176600) during the 1984 water year.

Table 15. Monthly loads and discharge for the River Raisin for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	14.98	1.206	27	371	2.8	1.26	21	9.6	703.7
Nov	54.45	1.427	26	4201	14.0	3.80	255	71.0	2247.0
Dec	130.92	1.153	25	6808	28.1	5.42	659	149.8	4066.7
Jan	28.02	0.956	27	46	2.7	1.31	50	27.4	1176.5
Feb	110.48	1.033	24	6779	21.7	4.79	413	129.1	2794.4
Mar	122.11	1.243	27	12894	34.9	4.44	500	203.6	3472.3
Apr	119.19	1.175	27	11895	27.3	2.70	580	166.8	3583.2
May	92.11	1.286	25	10440	25.7	2.67	485	124.7	2685.4
Jun	45.12	1.335	26	3332	9.2	1.40	170	47.6	1416.8
Jul	12.27	1.386	27	365	1.9	0.20	7	11.4	713.3
Aug	12.34	1.356	26	247	2.3	0.63	25	10.8	721.7
Sep	11.05	1.239	26	260	2.2	0.75	13	8.2	678.7
Totals	753.04		313	57636	172.8	29.37	3177	959.9	24259.7

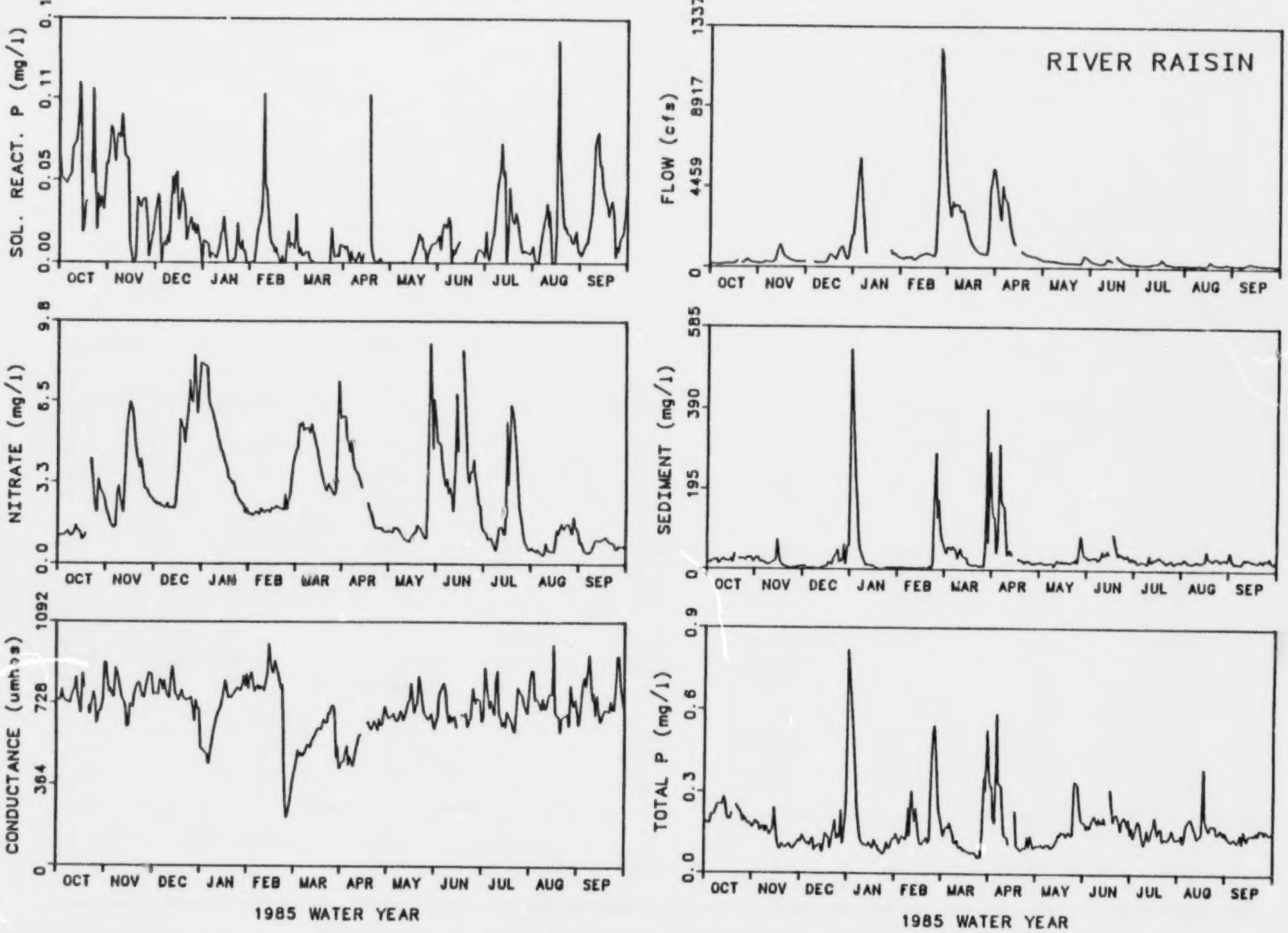

Figure 16. Annual hydrograph, sedigraph and nutrient chemograph for the River Raisin (USGS No. 04176600) during the 1985 water year.

Table 16. Monthly loads and discharge for the River Raisin for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	18.42	1.400	26	436	3.8	---	36	13.3	904.3
Nov	34.90	1.434	25	791	5.1	---	151	31.5	1581.7
Dec	48.76	1.178	29	3881	10.4	---	279	56.0	2235.4
Jan	112.93	1.441	26	10060	32.8	---	617	162.7	3910.0
Feb	140.34	0.968	24	16342	50.9	---	393	228.5	3384.1
Mar	201.38	1.209	28	16486	37.7	---	1024	261.3	5703.6
Apr	156.95	1.362	23	18940	44.6	---	696	216.9	3954.1
May	29.98	1.652	26	748	4.5	---	71	29.7	1325.1
Jun	27.20	1.475	26	1053	5.4	---	117	23.0	1182.8
Jul	17.65	1.515	24	429	2.7	---	45	16.5	818.3
Aug	14.08	1.373	28	375	2.5	---	15	13.1	744.3
Sep	14.14	1.430	25	356	2.0	---	11	10.4	715.5
Totals	816.73		310	69898	202.5	---	3454	1062.9	26459.2

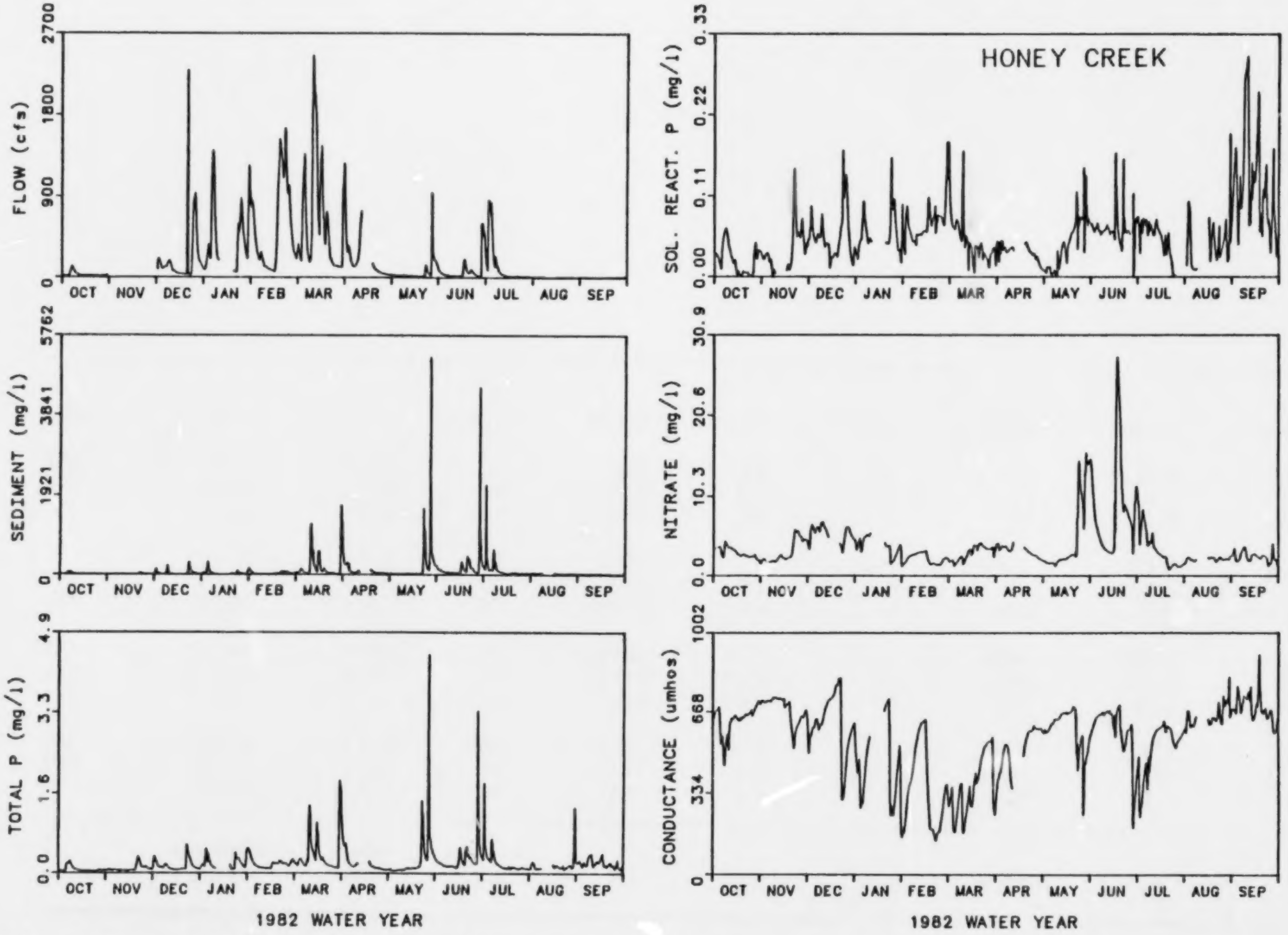

Figure 17. Annual hydrograph, sedigraph and nutrient chemograph for Honey Creek (USGS No. 04197100) during the 1982 water year.

Table 17. Monthly loads and discharge for Honey Creek at Melmore for water year 1982. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	1.89	1.012	35	49	0.2	0.07	6	1.7	41.2
Nov	4.15	1.012	35	47	0.6	0.24	19	4.4	143.7
Dec	13.44	0.878	43	554	2.4	0.97	79	14.5	424.9
Jan	18.93	0.703	41	944	5.0	1.26	68	26.1	373.5
Feb	30.69	0.826	39	1295	6.8	2.36	55	34.8	388.2
Mar	48.98	1.045	64	18023	28.5	2.37	129	115.4	673.9
Apr	19.45	1.502	42	5786	11.2	0.72	72	42.1	383.2
May	4.44	1.030	60	5272	5.3	0.28	41	19.6	93.0
Jun	6.02	1.105	61	4240	4.7	0.37	62	15.9	114.7
Jul	9.35	1.033	56	3502	4.8	0.63	63	19.9	118.5
Aug	0.19	1.424	28	5	<1.0	0.01	<1	0.1	5.7
Sep	0.16	0.518	34	3	<1.0	0.02	<1	0.2	5.3
Totals	157.70		538	39719	69.6	9.30	595	294.6	2765.9

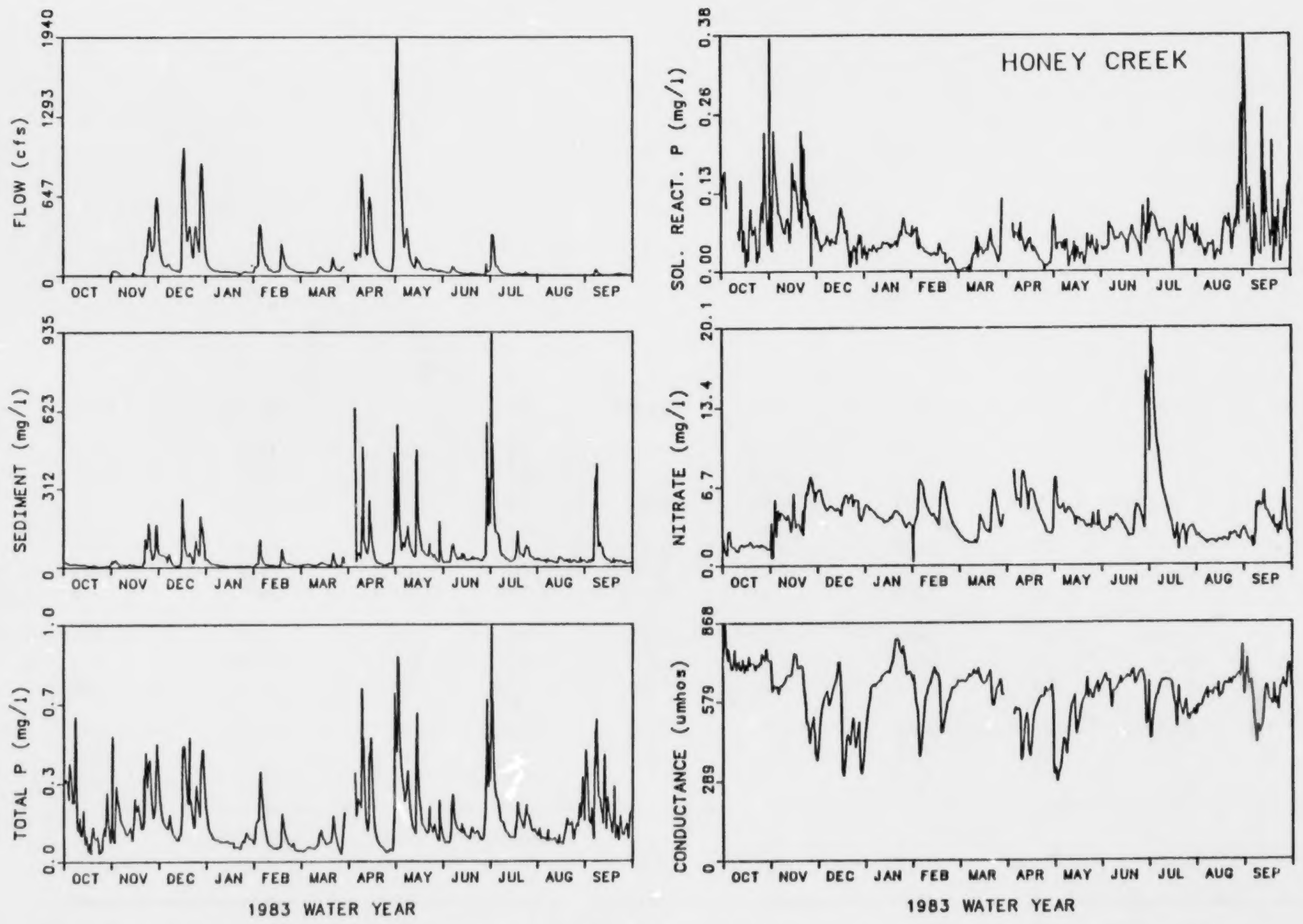

Figure 18. Annual hydrograph, sedigraph and nutrient chemograph for Honey Creek (USGS No. 04197100) during the 1983 water year.

Table 18. Monthly loads and discharge for Honey Creek at Melmore for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.13	0.615	35	1	<0.1	0.01	<1	0.1	4.8
Nov	7.99	1.010	62	779	2.8	0.77	49	12.4	236.1
Dec	21.98	1.040	55	2132	7.5	1.30	112	35.3	478.0
Jan	2.94	1.050	38	28	0.3	0.13	12	1.9	87.5
Feb	7.11	1.079	36	249	1.3	0.28	41	7.2	181.2
Mar	3.66	1.229	33	63	0.4	0.14	14	2.9	117.0
Apr	15.39	1.167	41	2190	5.2	0.75	95	25.2	300.8
May	23.81	1.021	52	5134	12.0	1.22	130	53.9	388.4
Jun	1.74	1.119	40	152	0.3	0.10	8	1.8	42.8
Jul	3.23	1.105	45	1029	1.5	0.24	44	6.8	67.6
Aug	0.18	1.246	36	4	<0.1	0.01	<1	0.1	4.6
Sep	0.56	0.993	39	76	0.2	0.04	2	0.7	15.0
Totals	88.73		512	11838	31.5	5.01	508	148.3	1923.9

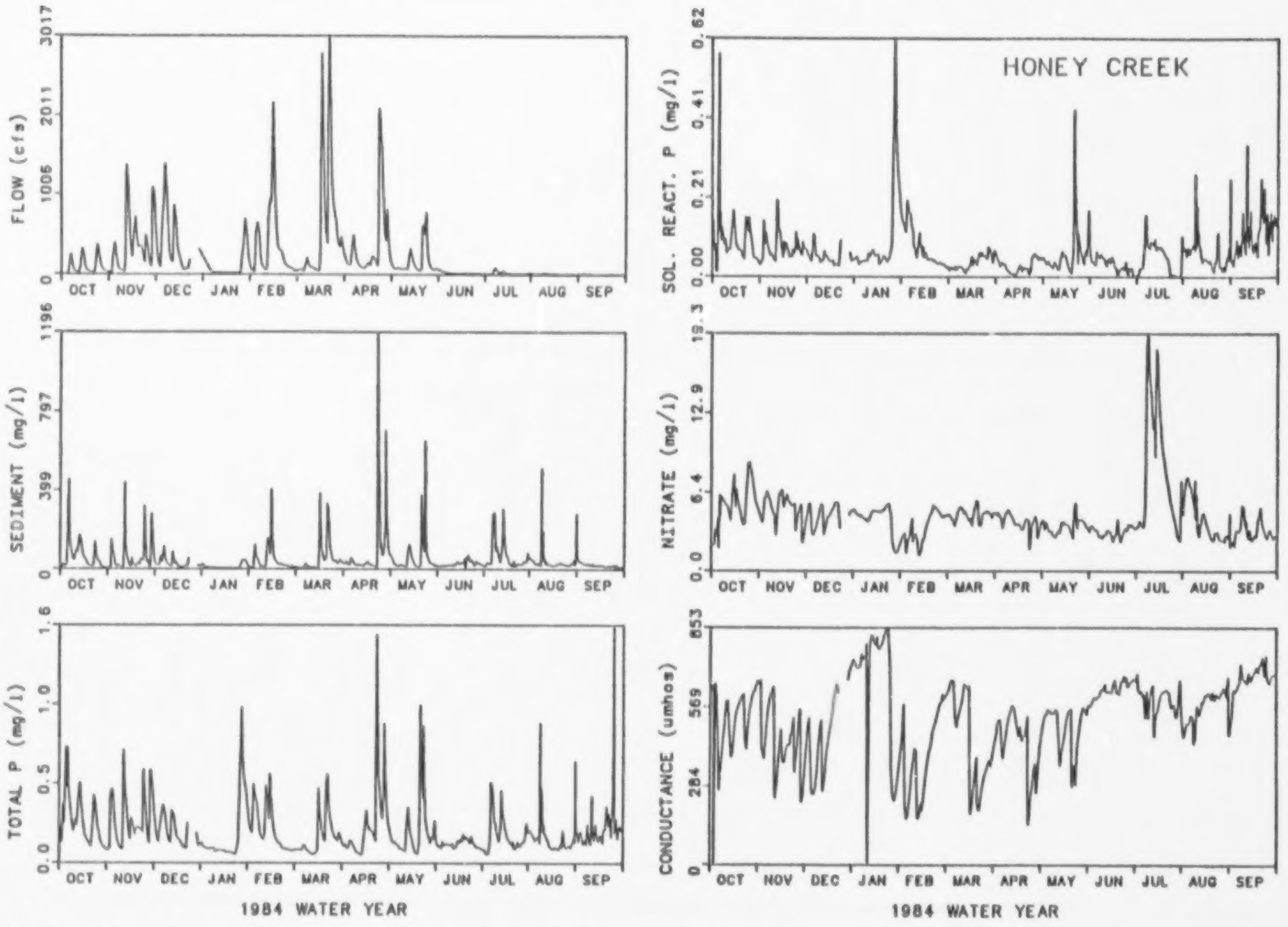

Figure 19. Annual hydrograph, sedigraph and nutrient chemograph for Honey Creek (USGS No. 04197100) during the 1984 water year.

Table 19. Monthly loads and discharge for Honey Creek at Melmore for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	7.57	1.096	40	783	2.8	0.89	50	12.3	155.8
Nov	30.46	1.035	48	2980	12.1	2.91	144	47.6	585.1
Dec	23.01	1.023	27	1148	6.4	1.35	90	27.1	372.0
Jan	4.72	0.617	34	146	2.3	1.28	12	9.1	92.4
Feb	17.09	0.621	38	1999	6.1	1.38	49	28.5	213.3
Mar	44.33	0.998	46	6044	14.1	2.24	195	63.8	542.6
Apr	24.98	0.906	41	6154	13.3	0.97	90	46.5	293.6
May	12.53	1.046	40	1863	5.1	1.38	50	19.5	216.5
Jun	1.25	1.369	34	28	0.2	0.05	4	1.0	27.4
Jul	1.54	1.251	39	236	0.5	0.13	19	2.4	45.5
Aug	0.52	1.773	59	35	0.1	0.04	2	0.5	13.2
Sep	0.20	0.659	35	4	<0.1	0.02	<1	0.2	8.0
Totals	168.21		481	21419	63.0	12.65	707	258.6	2565.5

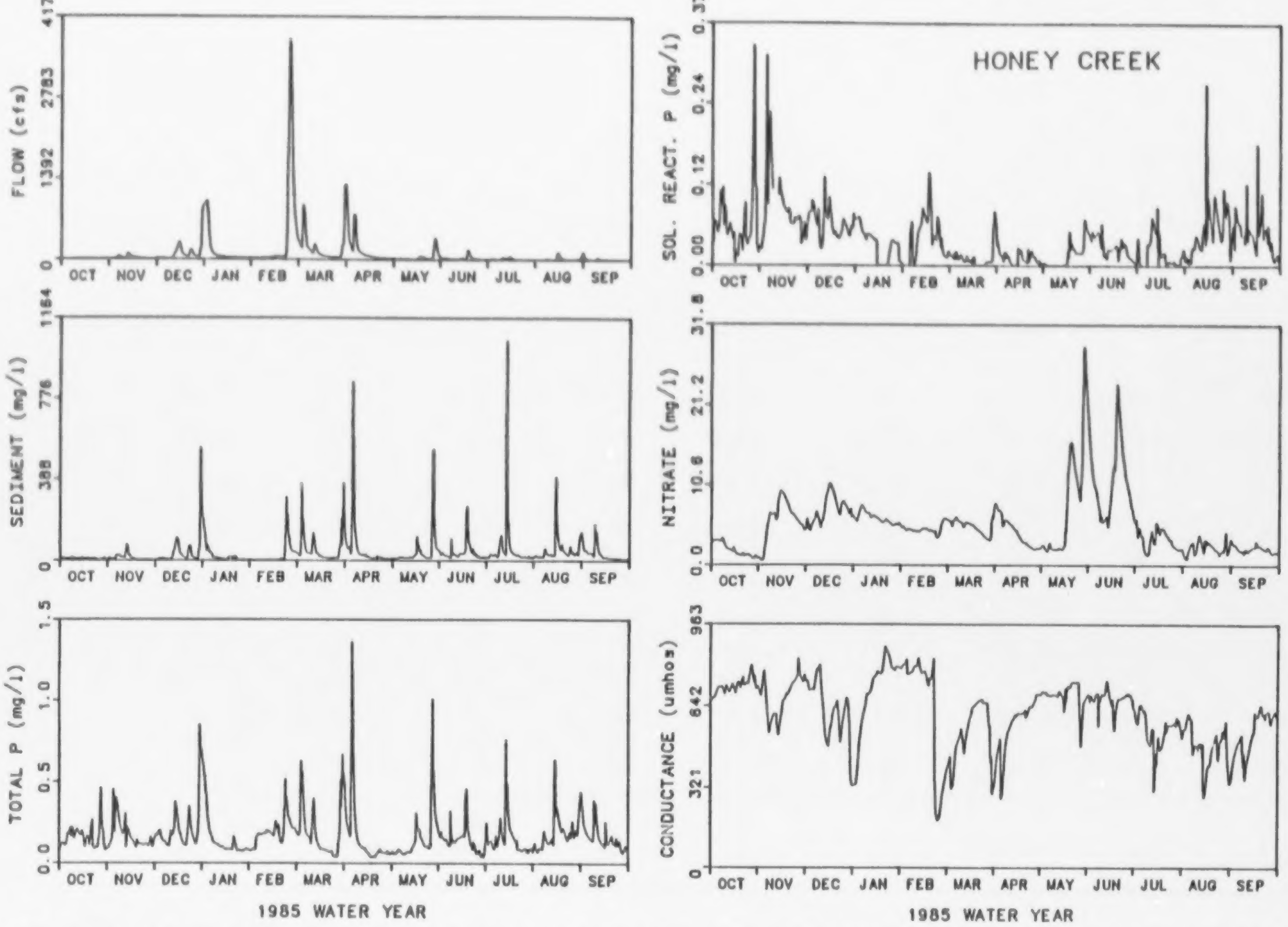

Figure 20. Annual hydrograph, sedigraph and nutrient chemograph for Honey Creek (USGS No. 04197100) during the 1985 water year.

Table 20. Monthly loads and discharge for Honey Creek at Melmore for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.68	1.163	36	5	0.1	---	1	0.6	23.8
Nov	2.16	1.212	34	55	0.4	---	15	2.5	75.3
Dec	10.92	1.148	36	1739	4.6	---	85	20.0	326.8
Jan	9.47	1.398	33	515	3.1	---	60	14.1	222.9
Feb	29.82	0.949	41	3227	8.6	---	136	46.1	452.2
Mar	15.15	1.020	46	1957	5.1	---	86	23.3	320.8
Apr	13.77	0.995	46	2657	6.6	---	89	28.9	257.3
May	3.41	1.051	43	595	1.5	---	62	6.4	118.7
Jun	2.28	1.284	45	224	0.5	---	35	2.7	74.8
Jul	1.00	1.291	41	136	0.3	---	4	1.4	23.8
Aug	2.00	1.319	41	276	0.7	---	6	2.8	35.8
Sep	0.77	1.390	40	53	0.2	---	2	0.9	14.9
Totals	91.43		482	11439	31.8	---	580	149.7	1947.2

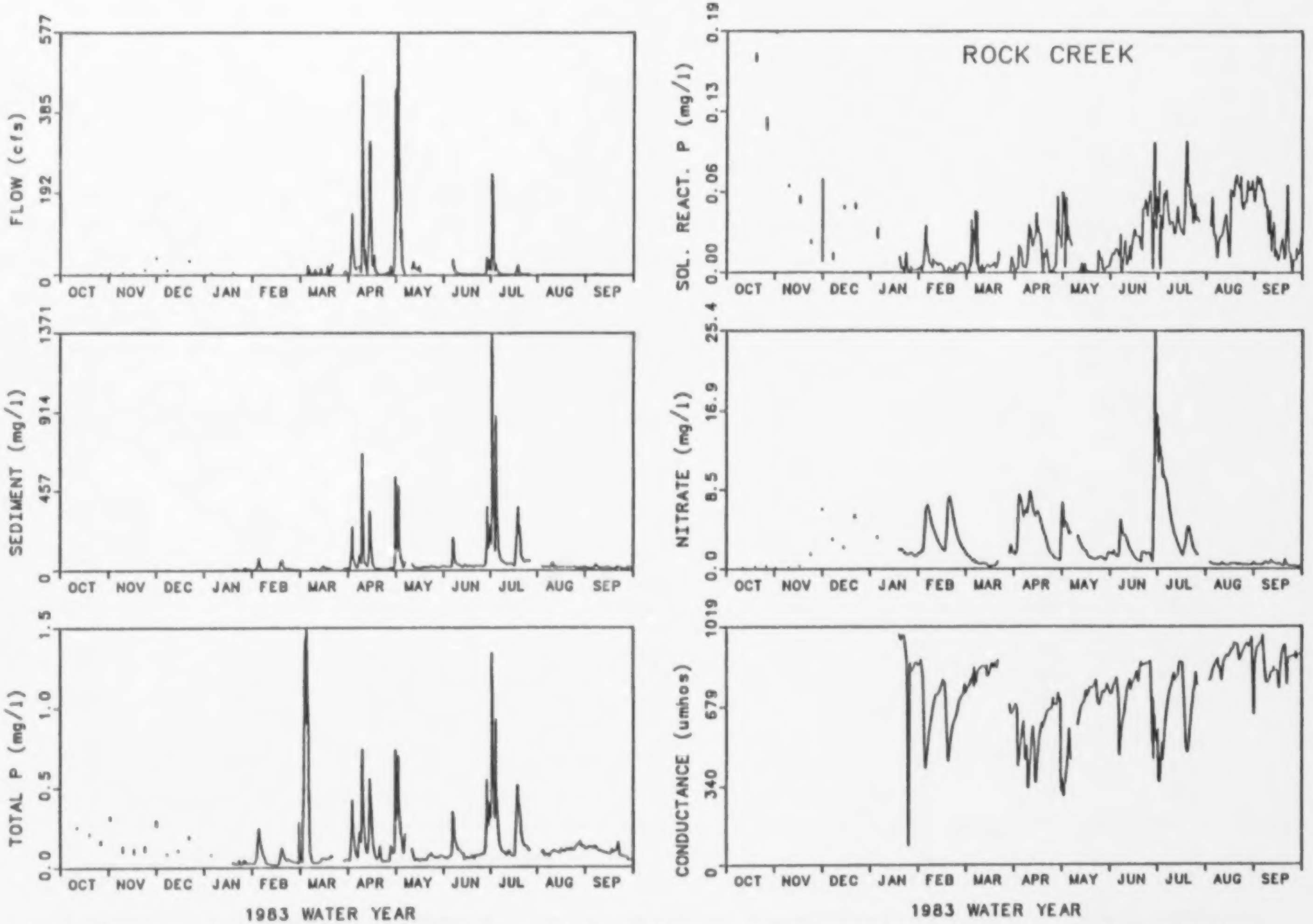

Figure 21. Annual hydrograph, sedigraph and nutrient chemograph for Rock Creek (USGS No. 04197170) during the 1983 water year.

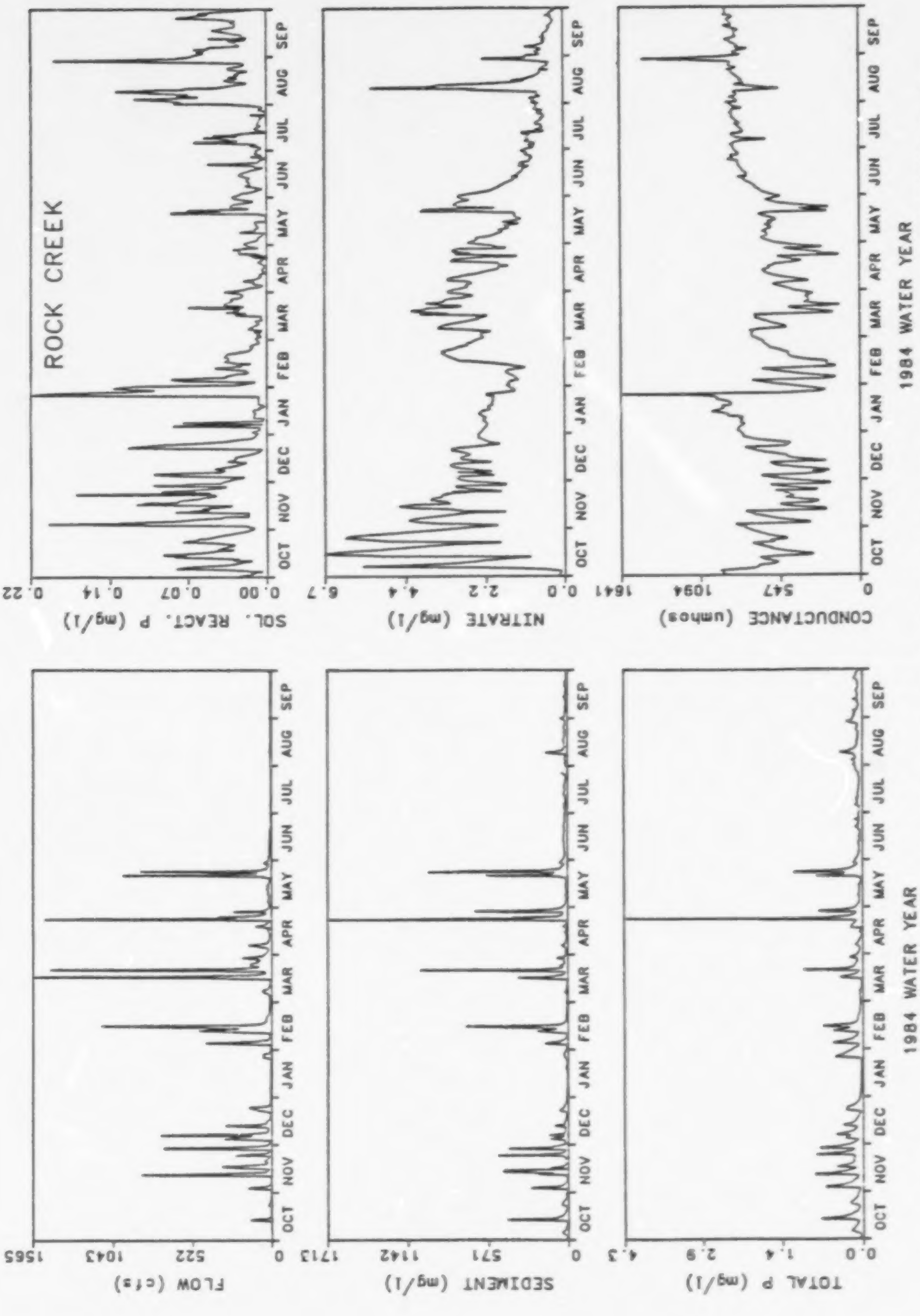

Figure 22. Annual hydrograph, sedigraph and nutrient chemograph for Rock Creek (USGS No. 04197170) during the 1984 water year.

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Table 22. Monthly loads and discharge for Rock Creek for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.91	1.199	39	141	0.35	0.062	4.5	1.50	22.8
Nov	7.30	0.948	51	1184	3.90	0.601	20.1	15.55	116.6
Dec	5.62	1.076	33	454	1.80	0.318	12.8	6.27	81.4
Jan	0.88	1.290	35	17	0.24	0.109	1.6	1.34	31.2
Feb	5.49	0.722	33	1703	2.53	0.213	10.1	12.86	65.3
Mar	10.46	0.769	65	2377	3.75	0.330	33.9	16.34	127.0
Apr	6.48	0.851	69	3276	4.80	0.064	14.6	15.73	66.5
May	4.72	0.722	54	1538	2.60	0.214	13.2	11.93	72.8
Jun	0.53	0.845	34	13	0.04	0.008	0.9	0.27	12.7
Jul	0.29	3.017	36	6	0.03	0.005	0.2	0.15	8.2
Aug	0.27	0.895	40	10	0.04	0.017	0.4	0.24	10.8
Sep	0.18	0.644	34	2	0.02	0.007	0.1	0.09	6.1
Totals	43.13		523	10721	20.10	1.949	112.6	82.26	621.3

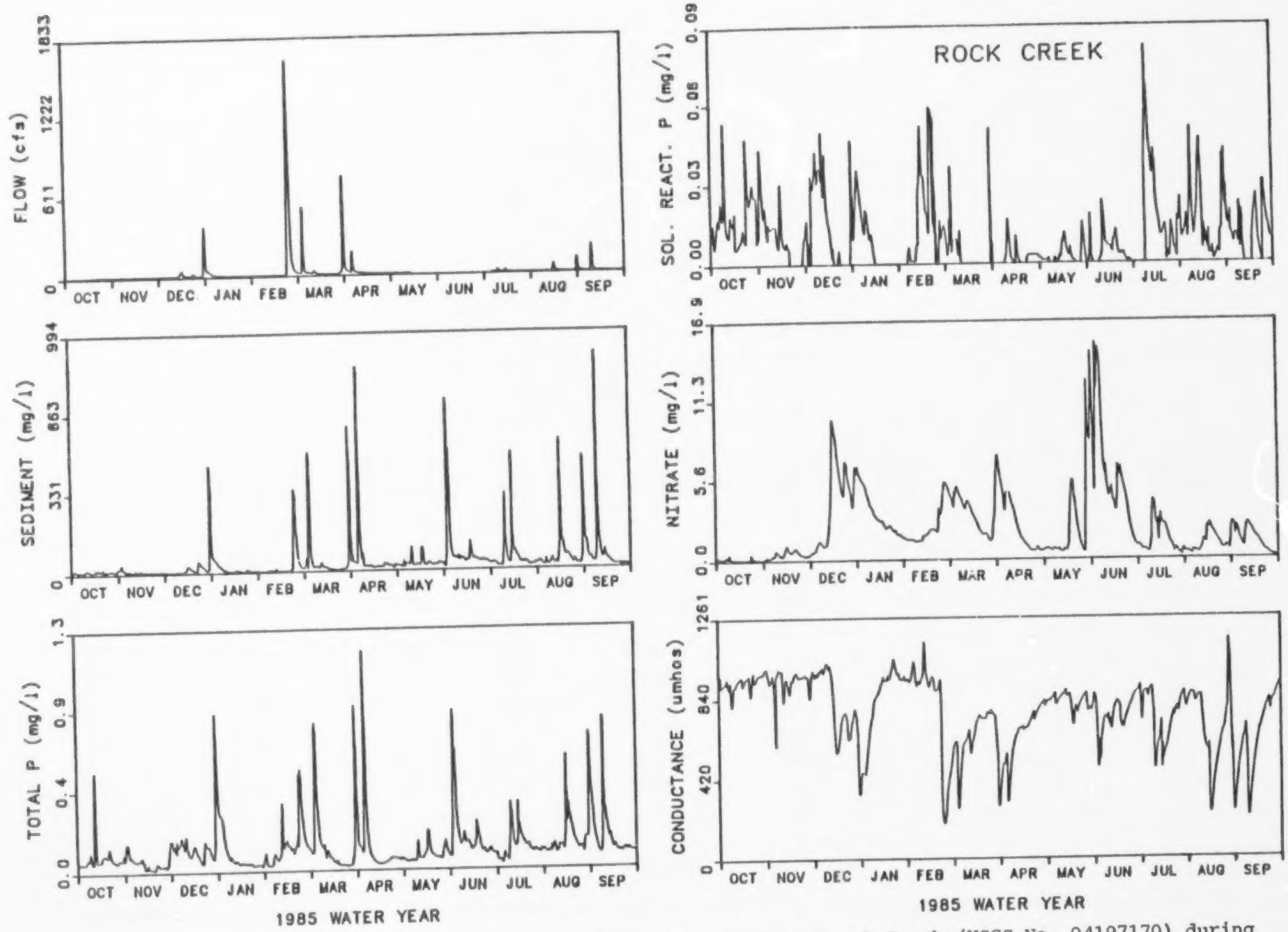

Figure 23. Annual hydrograph, sedigraph and nutrient chemograph for Rock Creek (USGS No. 04197170) during the 1985 water year.

Table 23. Monthly loads and discharge for Rock Creek for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.29	0.613	36	3	0.02	---	<0.1	0.10	9.4
Nov	0.37	0.620	34	3	0.02	---	0.2	0.16	16.3
Dec	1.86	0.865	47	296	0.75	---	10.7	3.69	70.3
Jan	1.55	2.155	33	21	0.14	---	5.2	0.93	59.5
Feb	7.57	0.889	81	1556	2.85	---	26.6	11.75	125.0
Mar	3.00	0.887	53	803	1.37	---	12.9	5.83	69.9
Apr	2.06	0.761	51	471	0.85	---	10.3	3.99	40.2
May	0.94	0.942	38	29	0.10	---	4.1	0.75	35.9
Jun	0.64	0.982	42	53	0.12	---	4.1	0.56	25.9
Jul	0.27	0.565	42	23	0.04	---	0.5	0.23	8.7
Aug	0.56	0.720	44	120	0.20	---	0.8	0.80	12.7
Sep	0.73	0.822	40	243	0.30	---	1.3	1.50	11.9
Totals	19.83		541	3621	6.76	---	76.6	30.28	485.6

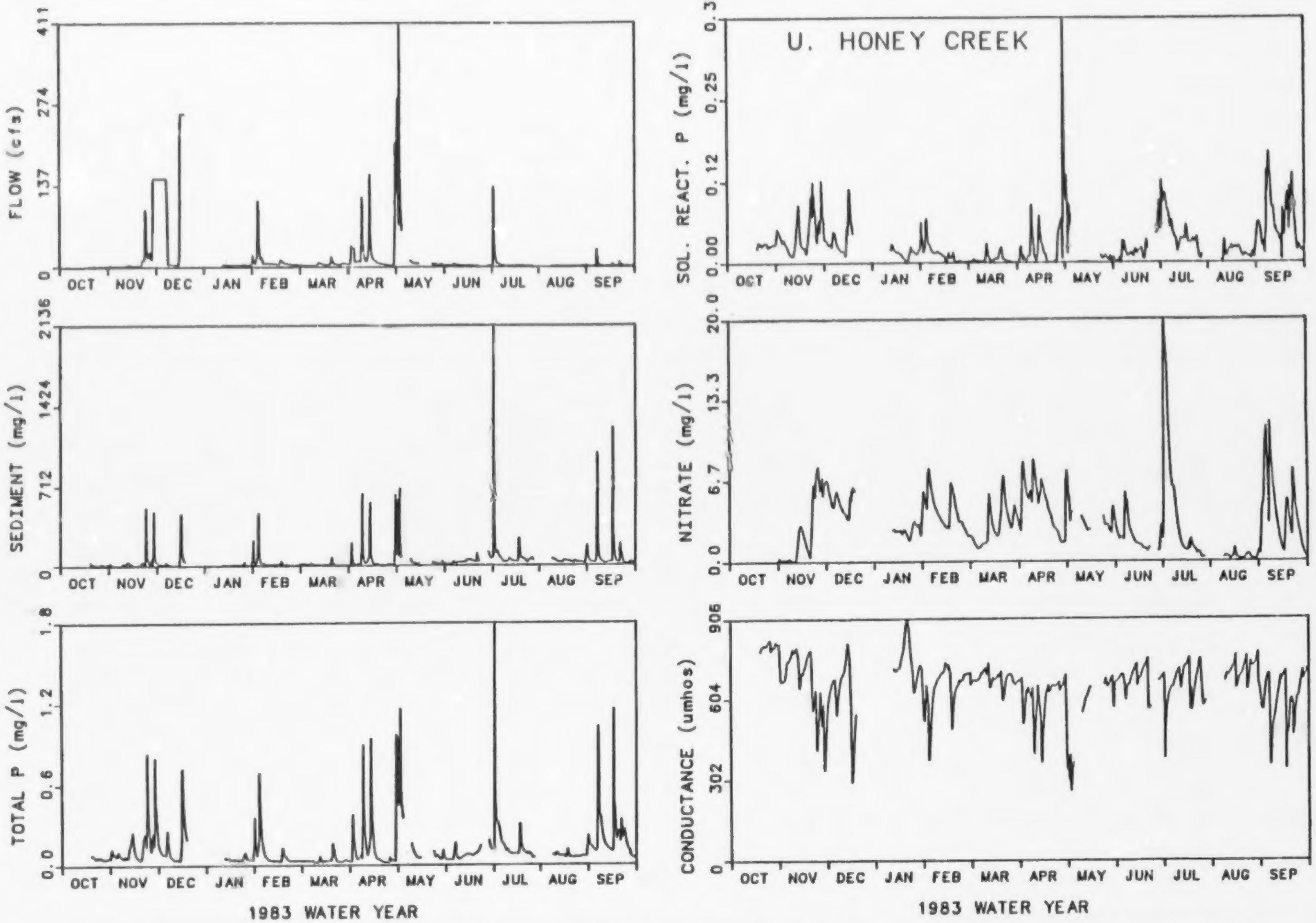

Figure 24. Annual hydrograph, sedigraph and nutrient chemograph for Upper Honey Creek (USGS No. 04197020) during the 1983 water year.

Table 24. Monthly loads and discharge for Upper Honey Creek for water year 1983. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.03	1.235	14	<1	<0.01	0.001	<0.1	0.02	0.7
Nov	1.41	1.154	54	171	0.51	0.108	8.6	2.58	41.3
Dec	2.58	0.528	29	154	0.58	0.130	14.4	3.31	78.3
Jan	0.28	1.480	23	9	0.03	0.006	0.9	0.15	9.6
Feb	0.85	1.292	37	93	0.20	0.025	4.7	0.95	22.0
Mar	0.56	1.777	35	8	0.03	0.004	2.1	0.30	18.5
Apr	1.77	1.481	51	288	0.60	0.077	10.9	3.50	40.1
May	2.71	1.381	32	859	1.81	0.237	13.4	7.35	45.2
Jun	0.21	1.670	29	7	0.02	0.004	0.5	0.14	6.1
Jul	0.45	1.338	36	299	0.32	0.036	5.9	1.38	9.4
Aug	0.01	0.678	26	1	<0.01	<0.001	<0.1	0.01	0.3
Sep	0.20	1.532	46	50	0.09	0.018	1.1	0.31	4.3
Totals	11.07		415	1939	4.17	0.645	62.4	20.00	276.0

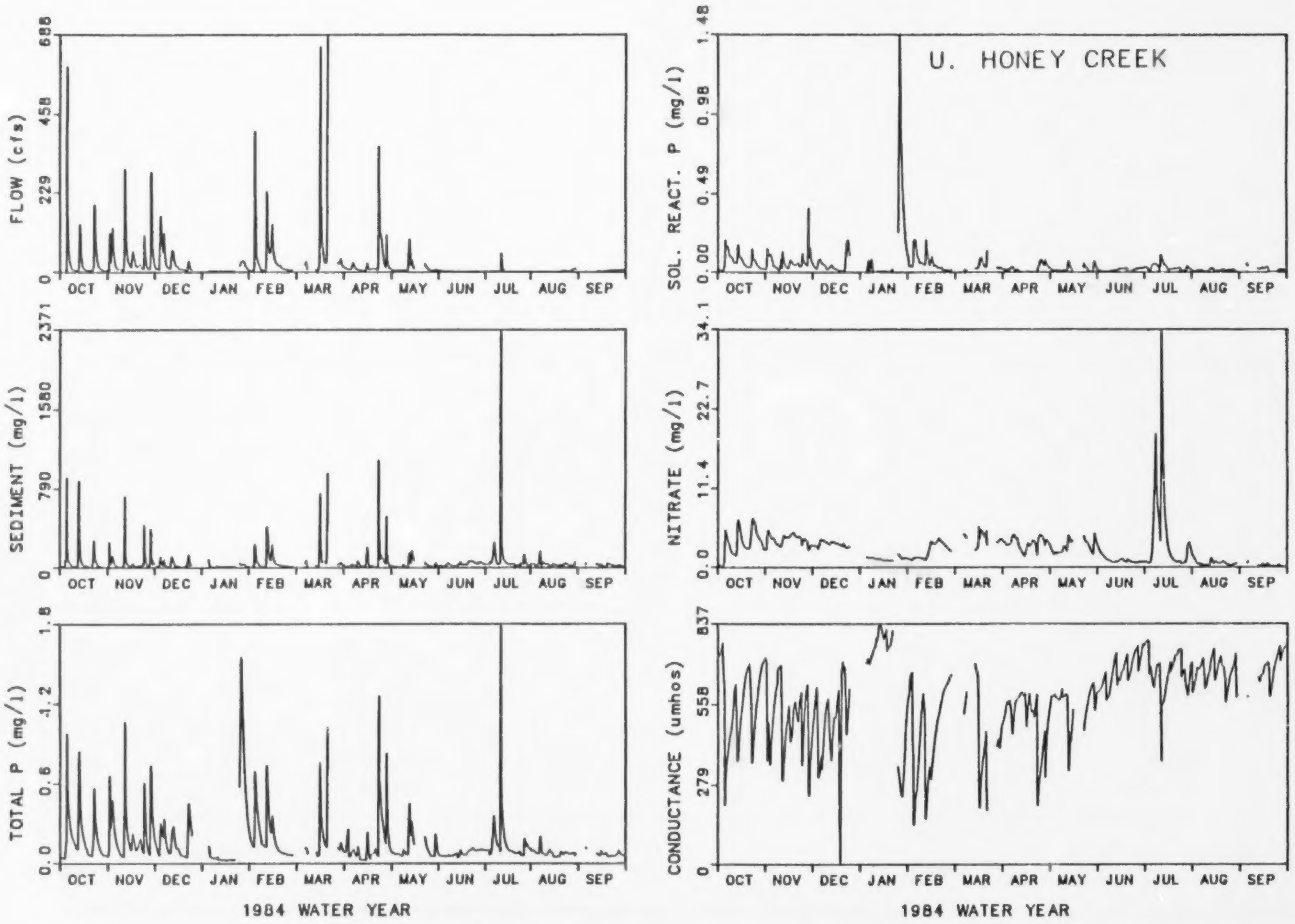

Figure 25. Annual hydrograph, sedigraph and nutrient chemograph for Upper Honey Creek (USGS No. 04197020) during the 1984 water year.

Table 25. Monthly loads and discharge for Upper Honey Creek for water year 1984. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	2.72	1.200	43	569	1.34	0.323	14.0	5.43	45.3
Nov	4.13	1.317	47	614	1.81	0.362	16.1	7.54	72.9
Dec	2.13	1.260	27	139	0.52	0.128	7.1	2.06	39.7
Jan	0.35	0.792	29	9	0.26	0.187	0.5	0.78	8.0
Feb	2.03	0.840	38	353	0.90	0.228	4.3	3.95	28.5
Mar	4.83	1.355	24	1874	2.70	0.385	20.0	9.66	59.8
Apr	2.43	1.376	41	550	1.17	0.083	9.1	4.23	33.0
May	1.88	2.838	28	151	0.48	0.074	7.0	2.55	38.0
Jun	0.19	2.722	34	6	0.01	0.002	0.2	0.08	4.8
Jul	0.30	2.046	42	205	0.21	0.017	5.1	0.70	8.2
Aug	0.04	0.420	32	1	<0.01	<0.001	<0.1	0.02	1.0
Sep	0.03	0.196	24	<1	<0.01	<0.001	<0.1	0.01	0.9
Totals	21.07		409	4472	9.42	1.790	83.4	36.99	340.0

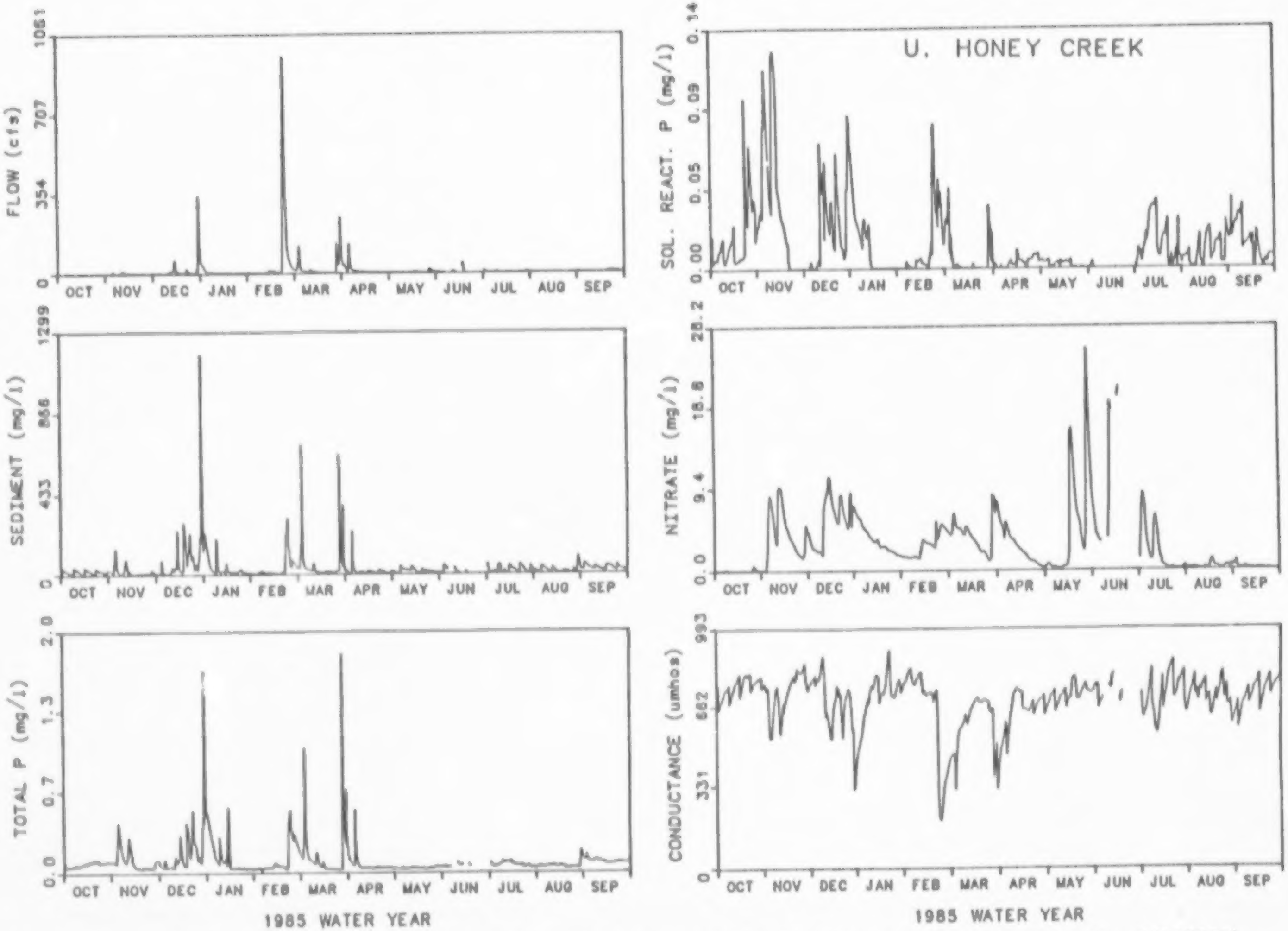

Figure 26. Annual hydrograph, sedigraph and nutrient chemograph for Upper Honey Creek (USGS No. 04197020) during the 1985 water year.

Table 26. Monthly loads and discharge for Upper Honey Creek for water year 1985. Discharge is given in million cubic meters, and loads are given in metric tons.

Month	USGS Discharge	Flow Ratio	N of Samples	SS	TP	SRP	NO23-N	TKN	CL
Oct	0.04	0.844	36	1	<0.01	---	<0.1	0.01	0.8
Nov	0.37	2.145	35	15	0.07	---	2.4	0.42	11.8
Dec	1.72	1.419	41	923	1.47	---	11.7	4.37	39.2
Jan	0.85	2.893	33	76	0.20	---	4.2	0.89	24.3
Feb	4.50	0.957	44	816	1.69	---	19.1	6.32	67.1
Mar	2.09	1.380	50	391	0.97	---	12.7	4.37	50.0
Apr	1.42	1.629	39	59	0.22	---	7.3	1.43	36.6
May	0.42	2.374	34	4	0.02	---	4.3	0.23	16.9
Jun	0.46	2.258	14	6	0.03	---	7.7	0.09	17.1
Jul	0.15	1.044	34	4	0.01	---	0.3	0.06	5.1
Aug	0.04	0.916	35	1	<0.01	---	<0.1	0.02	1.4
Sep	0.02	0.109	34	<1	<0.01	---	<0.1	0.01	0.4
Totals	12.07		429	2296	4.68	---	69.7	18.23	270.7

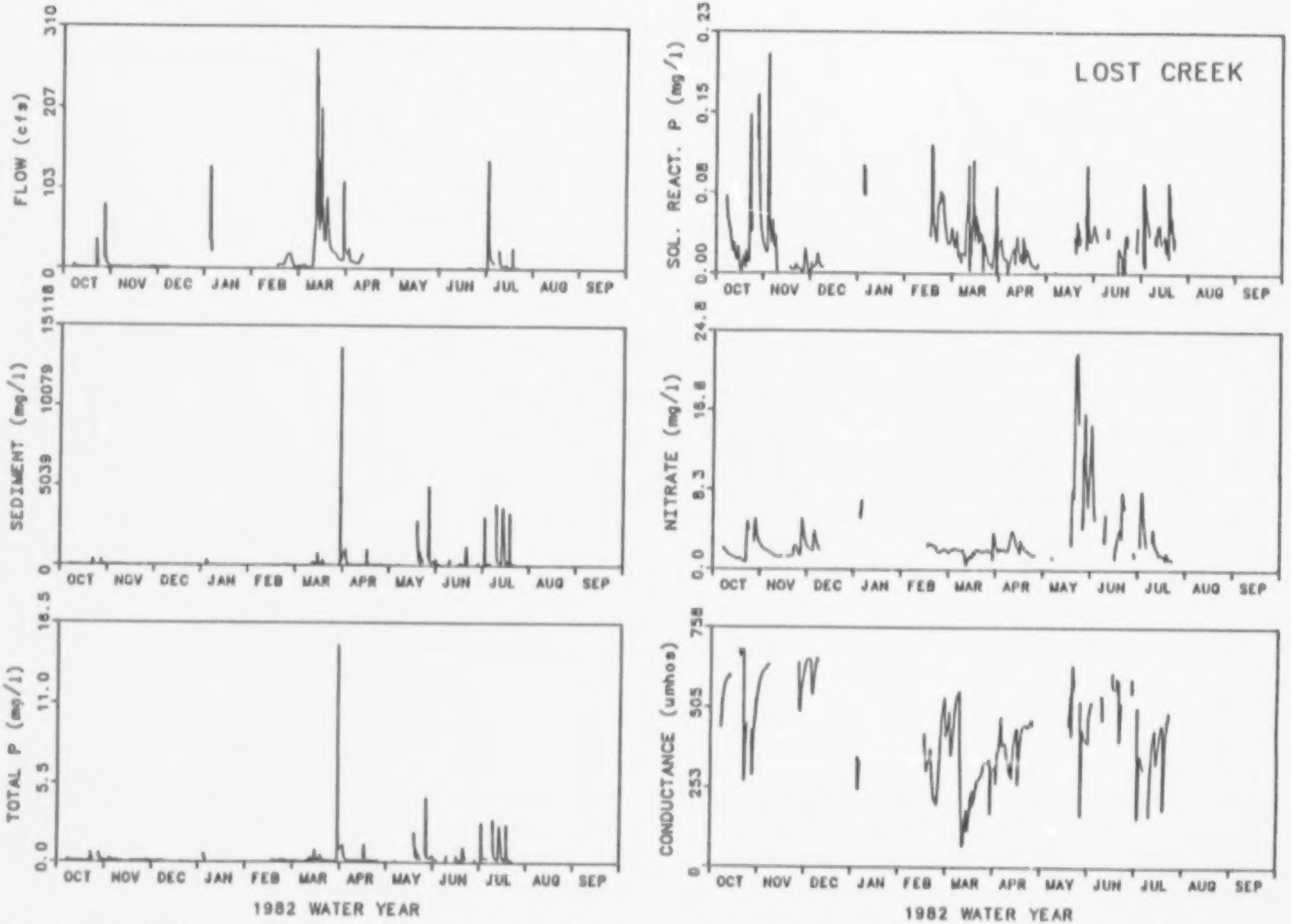

Figure 27. Annual hydrograph, sedigraph and nutrient chemograph for Lost Creek (USGS No.04185440) during the 1982 water year.

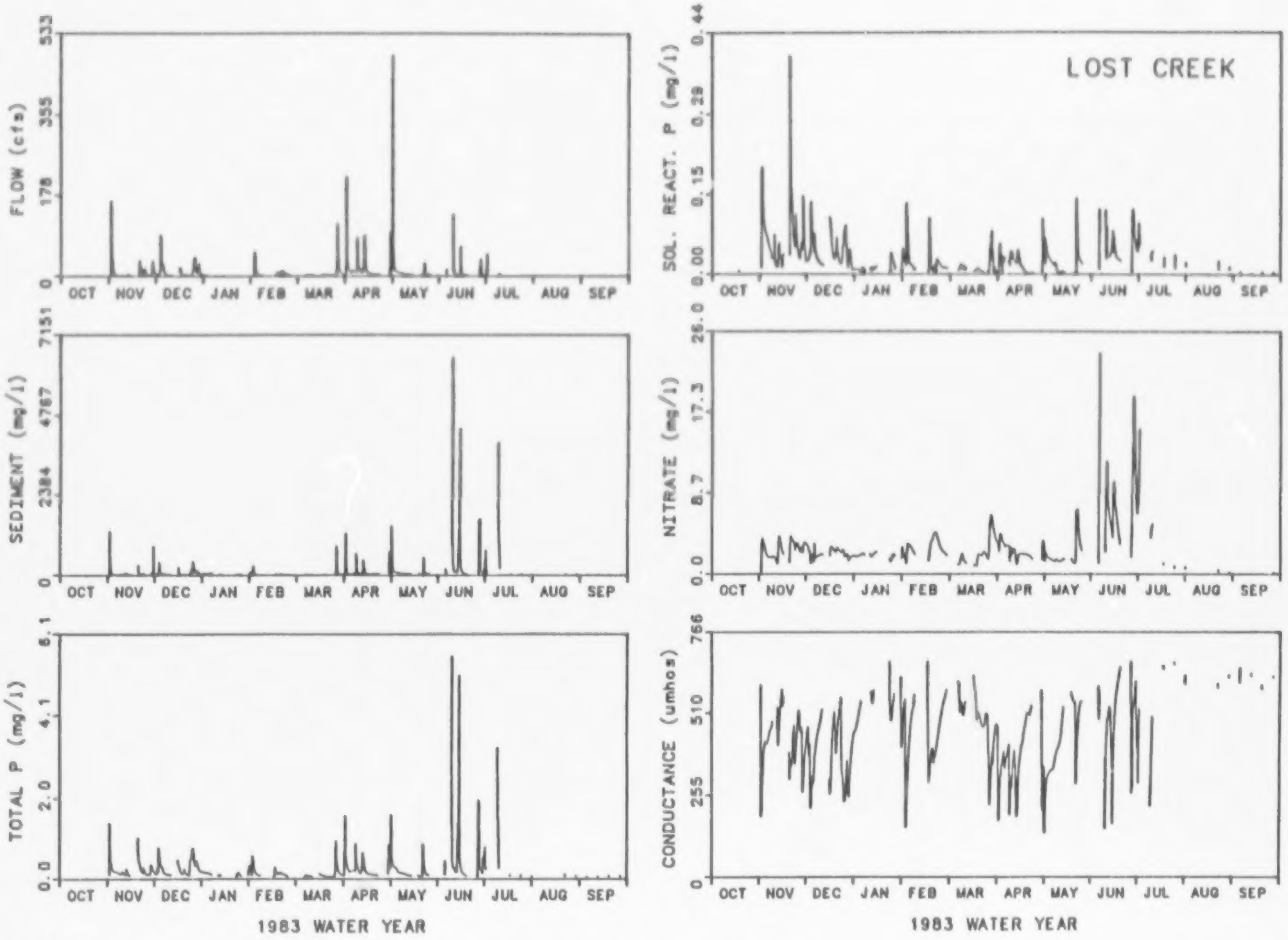

Figure 28. Annual hydrograph, sedigraph and nutrient chemograph for Lost Creek (USGS No.04185440) during the 1983 water year.

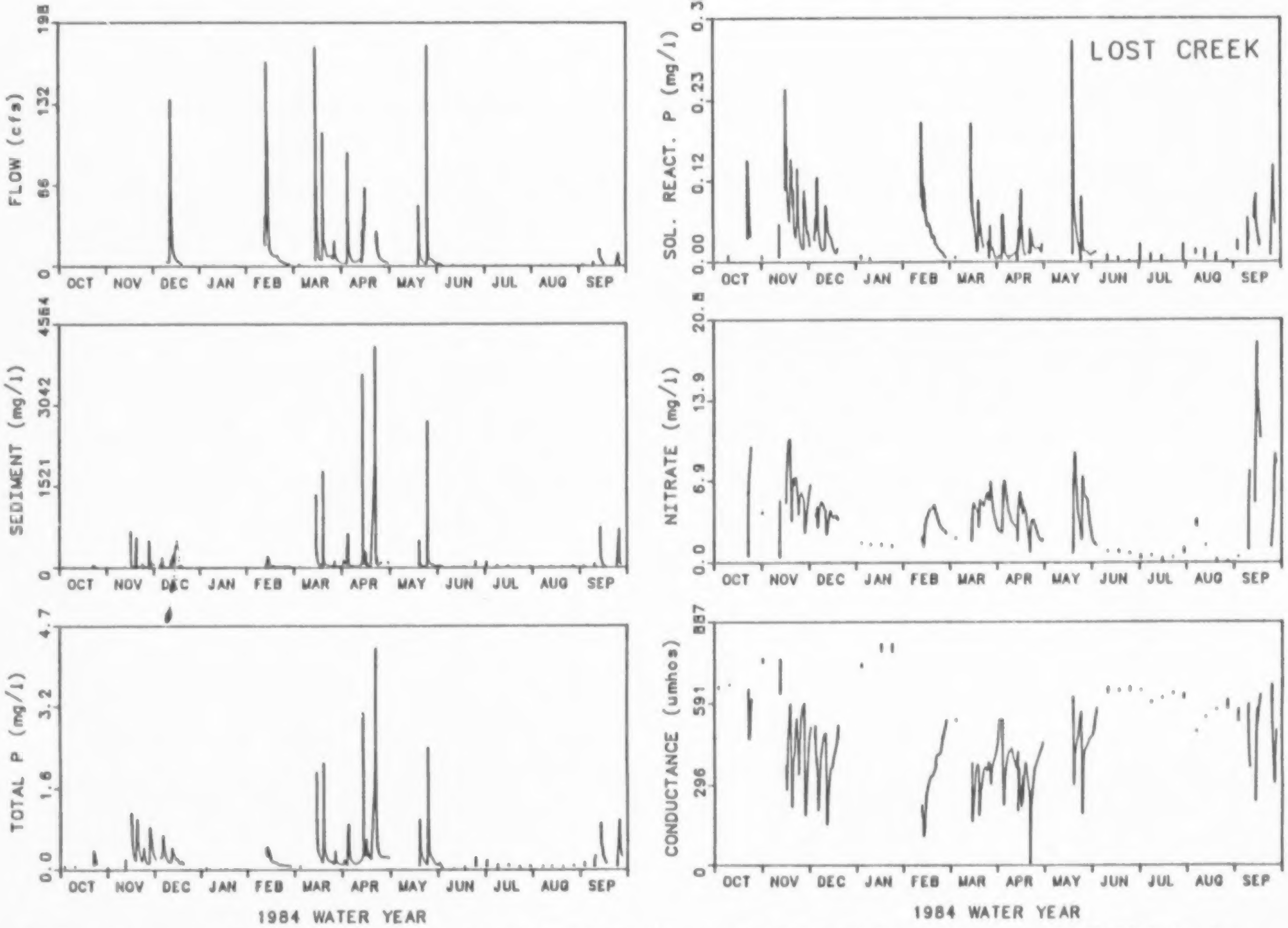

Figure 29. Annual hydrograph, sedigraph and nutrient chemograph for Lost Creek (USGS No.04185440) during the 1984 water year.

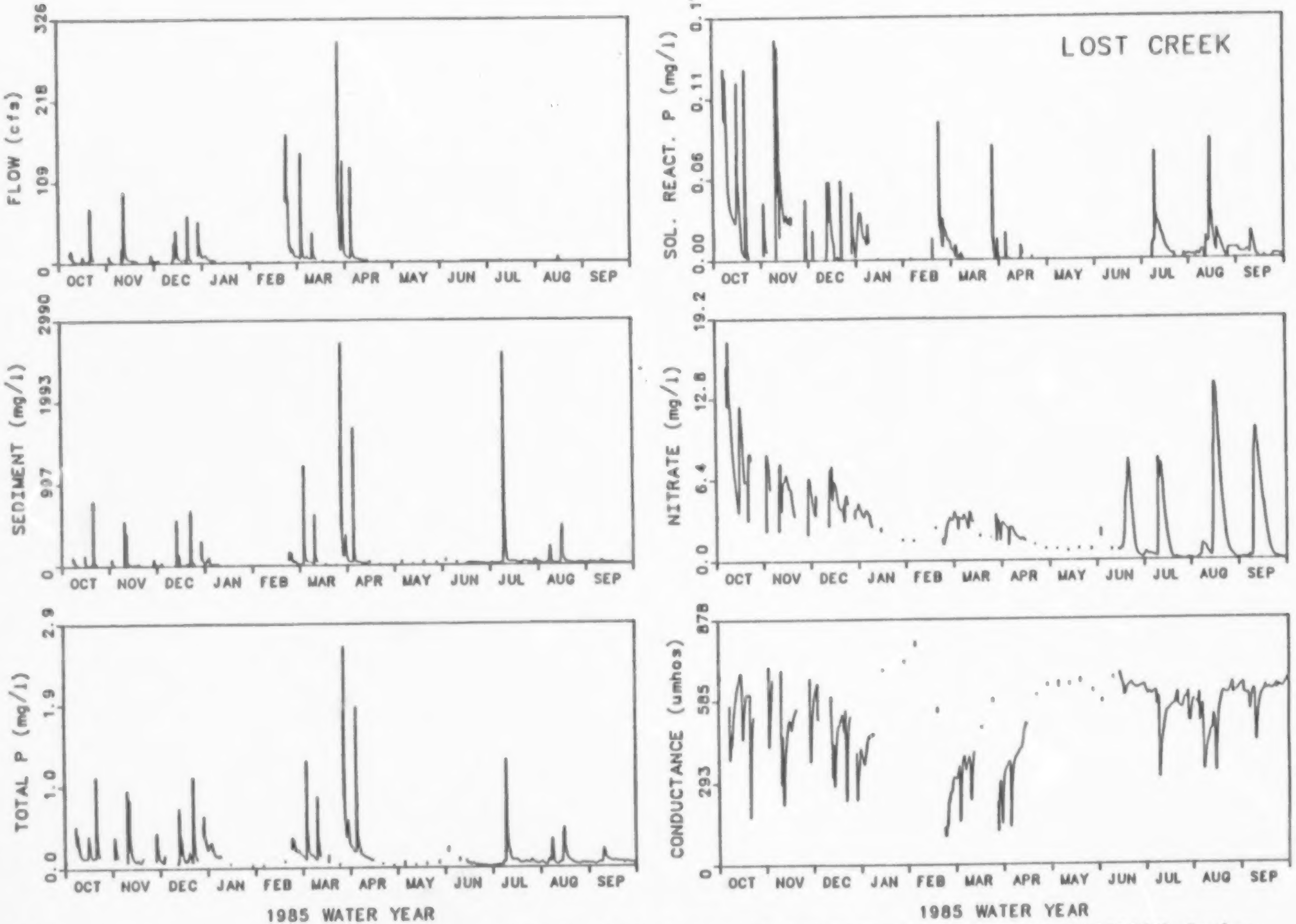

Figure 30. Annual hydrograph, sedigraph and nutrient chemograph for Lost Creek (USGS No.04185440) during the 1985 water year.

APPENDIX 2

TIME WEIGHTED MEAN PESTICIDE CONCENTRATIONS AND PESTICIDE LOADINGS AT LAKE ERIE TRIBUTARY MONITORING STATIONS: 1983 - 1985 WATER YEARS

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APPENDIX 2 -- NOTES

Contents

This Appendix contains a summary of the time weighted mean pesticide concentrations, the pesticide loads, and the unit area pesticide loads for Lake Erie tributary monitoring stations during the 1983, 1984 and 1985 water years. The Appendix is organized such that the time weighted mean concentrations and the loading data for a particular station and year are presented on facing pages. The methods of calculation for time weighted mean concentrations and pesticide loads are presented in the accompanying report.

Additional Parameters

In addition to the pesticides for which calculations are included in this Appendix, samples were also analyzed for several other pesticides. These are listed in the TWMC tables. Since they were rarely detected, calculation of concentrations and loads are not included in the Appendix.

Data Availability

Data containing the concentrations of pesticides in individual samples are available in the U.S. EPA's STORET data system. The data are stored under the corresponding U.S. Geological Survey station number. Data can also be supplied directly on magnetic tape from the Water Quality Laboratory, Heidelberg College, Tiffin, Ohio 44883.

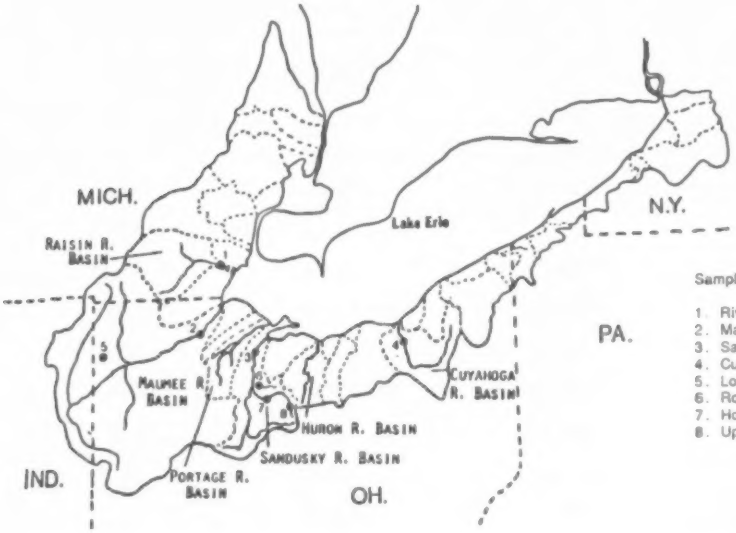
Sampling and Analytical Methods and Calculational Procedures

The sampling methods, analytical procedures and calculational methods are described in the accompanying main report. The analytical procedure has also been described in detail in the following paper:

> Kramer, Jack W. and David B. Baker. 1985. An analytical method and quality control program for studies of currently used pesticides in surface waters. IN: Taylor, J.K. and T.W. Stanley, eds. Quality assurance for environmental measurements, ASTM STP 867. Amer. Soc. Testing & Materials, Philadelphia. pp. 116-132.

Sampling Locations

Locations of Lake Erie Tributary monitoring stations operated by the Water Quality Laboratory at Heidelberg College for the 1982-1985 water years are shown below:


MICH.
Lake Erie
N.Y.
RAISIN R. BASIN
PA.
MAUMEE R. BASIN
CUYAHOGA R. BASIN
HURON R. BASIN
SANDUSKY R. BASIN
PORTAGE R. BASIN
IND.
OH.
1
2
3
4
5
6
7
8

Sampling Locations:

1. River Raisin near Monroe, MI
2. Maumee R. at Bowling Green, OH water intake
3. Sandusky R. near Fremont, OH
4. Cuyahoga R. at Independence, OH
5. Lost Cr. tributary near Defiance, OH
6. Rock Cr. at Tiffin, OH
7. Honey Cr. at Melmore, OH
8. Upper Honey Cr. at New Washington, OH

List of Tables

Appendix II contains two types of tables. The first type presents the time weighted mean concentration (TWMC's) of pesticides for a particular station and water year. The second type presents the pesticide loads and unit area loads for each station and water year.

Table	Station	Type	Water Year	Page
1	Maumee	TWMC	1983	178
2	Maumee	Loads	1983	179
3	Maumee	TWMC	1984	180
4	Maumee	Loads	1984	181
5	Maumee	TWMC	1985	182
6	Maumee	Loads	1985	183
7	Sandusky	TWMC	1983	184
8	Sandusky	Loads	1983	185
9	Sandusky	TWMC	1984	186
10	Sandusky	Loads	1984	187
11	Sandusky	TWMC	1985	188
12	Sandusky	Loads	1985	189
13	Honey Creek	TWMC	1983	190
14	Honey Creek	Loads	1983	191
15	Honey Creek	TWMC	1984	192
16	Honey Creek	Loads	1984	193
17	Honey Creek	TWMC	1985	194
18	Honey Creek	Loads	1985	195
19	Upper Honey Creek	TWMC	1983	196
20	Upper Honey Creek	Loads	1983	197
21	Upper Honey Creek	TWMC	1984	198
22	Upper Honey Creek	Loads	1984	199
23	Upper Honey Creek	TWMC	1985	200
24	Upper Honey Creek	Loads	1985	201
25	Rock Creek	TWMC	1983	202
26	Rock Creek	Loads	1983	203
27	Rock Creek	TWMC	1984	204
28	Rock Creek	Loads	1984	205
29	Rock Creek	TWMC	1985	206
30	Rock Creek	Loads	1985	207

Table	Station	Type	Water Year	Page
31	Lost Creek	TWMC	1983	208
32	Lost Creek	Loads	1983	209
33	Lost Creek	TWMC	1984	210
34	Lost Creek	Loads	1984	211
35	Lost Creek	TWMC	1985	212
36	Lost Creek	Loads	1985	213
37	Raisin	TWMC	1983	214
38	Raisin	Loads	1983	215
39	Raisin	TWMC	1984	216
40	Raisin	Loads	1984	217
41	Raisin	TWMC	1985	218
42	Raisin	Loads	1985	219
43	Cuyahoga	TWMC	1983	220
44	Cuyahoga	Loads	1983	221
45	Cuyahoga	TWMC	1984	222
46	Cuyahoga	Loads	1984	223
47	Cuyahoga	TWMC	1985	224
48	Cuyahoga	Loads	1985	225

Table 1: Pesticide concentrations for the Maumee River in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 116
Results based on 43 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0000	0.0000	0
Carbofuran	0.1749	0.0585	20.2903
Atrazine	1.7507	0.5852	203.076
Terbufos	0.0008	0.0003	.09375
Fonofos	0.0000	0.0000	0
Metribuzin	0.4429	0.1481	51.3816
Alachlor	1.0461	0.3496	121.344
Linuron	0.0355	0.0119	4.1217
Metolachlor	1.3080	0.4372	151.73
Cyanazine	0.6616	0.2211	76.7448

Table 2: Pesticide loads for the Maumee River, USGS04193500, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 52 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	0	0	0
Carbofuran	235.161	249.423	.152134
Atrazine	2373.65	2517.61	1.53559
Terbufos	2.22466	2.35958	.143921E-02
Fonofos	0	0	0
Metribuzin	664.465	704.763	.429865
Alachlor	1948	2066.14	1.26023
Linuron	44.4298	47.1244	.287431E-01
Metolachlor	1678.25	1780.04	1.08572
Cyanazine	1103.59	1170.52	.713948
Pendimethalin	56.8027	60.2476	.367475E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 116.434 days.
The monitored discharge is 681260 cfs-days, or 1667.04 million cubic meters.

The total discharge during this time is 722577 cfs-days, or 1768.14 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 161 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 3: Pesticide concentrations for the Maumee River in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.488
Results based on 58 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1849	0.0618	22.2798
Carbofuran	0.1878	0.0628	22.6228
Atrazine	2.9754	0.9945	358.494
Terbufos	0.0003	0.0001	.032
Fonofos	0.0022	0.0007	.266094
Metribuzin	0.4484	0.1499	54.0253
Alachlor	1.7556	0.5868	211.524
Linuron	0.0396	0.0132	4.76666
Metolachlor	1.5738	0.5260	189.622
Cyanazine	1.1463	0.3831	138.114

Table 4: Pesticide loads for the Maumee River, USGS04193500, during the time interval 8404150000 to 8408150000, a span of 122 days, during which 67 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	287.449	290.954	.177465
Carbofuran	503.242	509.379	.310692
Atrazine	4749.82	4807.74	2.93245
Terbufos	.523548	.529933	.323228E-03
Fonofos	6.37051	6.44821	.393303E-02
Metribuzin	1794.54	1816.42	1.10791
Alachlor	5188.71	5251.98	3.20341
Linuron	54.3	54.9622	.335238E-01
Metolachlor	3019.99	3056.82	1.86448
Cyanazine	2854.17	2888.98	1.76211
Pendimethalin	117.083	118.511	.722849E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 119.009 days.
The monitored discharge is 729089 cfs-days, or 1784.08 million cubic meters.

The total discharge during this time is 737980 cfs-days, or 1805.84 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 122 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 173 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 5: Pesticide concentrations for the Maumee River in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.503
Results based on 38 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1653	0.0553	19.9206
Carbofuran	0.0461	0.0154	5.55576
Atrazine	1.9017	0.6356	229.164
Terbufos	0.0009	0.0003	.108242
Fonofos	0.0004	0.0001	.503646E-01
Metribuzin	0.2536	0.0848	30.561
Alachlor	0.4723	0.1578	56.908
Linuron	0.0126	0.0042	1.5225
Metolachlor	1.3159	0.4398	158.574
Cyanazine	0.3216	0.1075	38.7578

Table 6: Pesticide loads for the Maumee River, USGS04193500, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 42 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	66.0537	67.3255	.410647E-01
Carbofuran	26.8966	27.4145	.167213E-01
Atrazine	714.135	727.885	.443968
Terbufos	.33093	.337302	.205735E-03
Fonofos	.517415	.527378	.32167E-03
Metribuzin	123.306	125.68	.766574E-01
Alachlor	259.141	264.131	.161104
Linuron	19.4406	19.8149	.120859E-01
Metolachlor	607.037	618.725	.377387
Cyanazine	134.686	137.28	.837327E-01
Pendimethalin	0	0	0
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 115.816 days.
The monitored discharge is 149661 cfs-days, or 366.222 million cubic meters.

The total discharge during this time is 152543 cfs-days, or 373.273 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.75 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 139 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 7: Pesticide concentrations for the Sandusky River in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 122.198
Results based on 45 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0000	0.0000	0
Carbofuran	0.1542	0.0515	18.8382
Atrazine	1.8049	0.6033	220.557
Terbufos	0.0000	0.0000	0
Fonofos	0.0035	0.0012	.43177
Metribuzin	0.2955	0.0988	36.112
Alachlor	0.5077	0.1697	62.0349
Linuron	0.0880	0.0294	10.7554
Metolachlor	2.2521	0.7528	275.199
Cyanazine	0.4470	0.1494	54.6176

Table 8: Pesticide loads for the Sandusky River, USGS04198000, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 49 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	0	0	0
Carbofuran	34.7943	30.2541	.093377
Atrazine	563.198	489.709	1.51145
Terbufos	0	0	0
Fonofos	.141157	.122738	.378822E-03
Metribuzin	84.2416	73.2494	.226078
Alachlor	179.872	156.402	.482721
Linuron	26.6641	23.1848	.715582E-01
Metolachlor	635.118	552.245	1.70446
Cyanazine	98.6846	85.8078	.264839
Pendimethalin	4.15412	3.61207	.111484E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 117.453 days.
The monitored discharge is 123364 cfs-days, or 301.871 million cubic meters.

The total discharge during this time is 107267 cfs-days, or 262.481 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 115.25 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 162 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 9: Pesticide concentrations for the Sandusky River in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.49
Results based on 53 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1503	0.0502	18.1118
Carbofuran	0.1370	0.0458	16.5041
Atrazine	2.5254	0.8441	304.279
Terbufos	0.0000	0.0000	0
Fonofos	0.0000	0.0000	0
Metribuzin	0.3709	0.1240	44.69
Alachlor	1.2546	0.4193	151.166
Linuron	0.0033	0.0011	.393226
Metolachlor	2.7255	0.9110	328.394
Cyanazine	0.4858	0.1624	58.5347

Table 10: Pesticide loads for the Sandusky River, USGS04198000, during the time interval 8404150000 to 8408150000, a span of 122 days, during which 60 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	40.3723	40.6242	.125383
Carbofuran	65.8552	66.2662	.204525
Atrazine	656.49	660.587	2.03885
Terbufos	0	0	0
Fonofos	0	0	0
Metribuzin	108.259	108.935	.336218
Alachlor	439.937	442.683	1.3663
Linuron	1.34463	1.35302	.004176
Metolachlor	522.266	525.525	1.62199
Cyanazine	161.119	162.125	.500386
Pendimethalin	5.34462	5.37798	.165987E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 119.76 days.
The monitored discharge is 144723 cfs-days, or 354.138 million cubic meters.

The total discharge during this time is 145626 cfs-days, or 356.348 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.75 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 177 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 11: Pesticide concentrations for the Sandusky River in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.505
Results based on 62 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1970	0.0659	23.741
Carbofuran	0.1858	0.0621	22.3859
Atrazine	4.4201	1.4774	532.646
Terbufos	0.0011	0.0004	.13625
Fonofos	0.0044	0.0015	.530953
Metribuzin	0.9166	0.3064	110.456
Alachlor	1.8770	0.6274	226.186
Linuron	0.3254	0.1088	39.2176
Metolachlor	4.8239	1.6124	581.301
Cyanazine	0.6176	0.2064	74.4226

Table 12: Pesticide loads for the Sandusky River, USGS04198000, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 66 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	41.1518	41.5872	.128356
Carbofuran	37.0776	37.4699	.115648
Atrazine	833.711	842.532	2.60041
Terbufos	.355286	.359045	.110816E-02
Fonofos	.985262	.995686	.307311E-02
Metribuzin	236.898	239.404	.738901
Alachlor	491.222	496.42	1.53216
Linuron	80.9559	81.8124	.252508
Metolachlor	1019.64	1030.43	3.18033
Cyanazine	108.339	109.485	.337917
Pendimethalin	.285062	.288078	.889128E-03
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 115.845 days.
The monitored discharge is 54637.1 cfs-days, or 133.697 million cubic meters.

The total discharge during this time is 55215.2 cfs-days, or 135.112 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 174 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 13: Pesticide concentrations for Honey Creek in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 122.168
Results based on 57 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0000	0.0000	0
Carbofuran	0.1052	0.0352	12.8497
Atrazine	3.0290	1.0124	370.049
Terbufos	0.0005	0.0002	.640278E-01
Fonofos	0.0000	0.0000	0
Metribuzin	0.3532	0.1180	43.1452
Alachlor	1.3811	0.4616	168.725
Linuron	0.3323	0.1111	40.5968
Metolachlor	2.9892	0.9991	365.186
Cyanazine	0.6600	0.2206	80.6281

Table 14: Pesticide loads for Honey Creek, USGS04197100, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 59 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	0	0	0
Carbofuran	2.99224	3.02351	.783292E-01
Atrazine	76.749	77.5509	2.00909
Terbufos	.657169E-02	.664036E-02	.17203E-03
Fonofos	0	0	0
Metribuzin	8.09728	8.18188	.211966
Alachlor	31.489	31.818	.824301
Linuron	6.49241	6.56024	.169954
Metolachlor	59.8298	60.455	1.56619
Cyanazine	12.9188	13.0538	.338182
Pendimethalin	.338332	.341867	.885666E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 114.939 days.
The monitored discharge is 13501.1 cfs-days, or 33.0373 million cubic meters.

The total discharge during this time is 13642.2 cfs-days, or 33.3825 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.75 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 176 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 15: Pesticide concentrations for Honey Creek in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 117.003
Results based on 72 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0519	0.0174	6.07593
Carbofuran	0.2668	0.0892	31.2206
Atrazine	4.4613	1.4912	521.984
Terbufos	0.0000	0.0000	0
Fonofos	0.0000	0.0000	0
Metribuzin	0.2709	0.0905	31.6909
Alachlor	2.1238	0.7099	248.492
Linuron	0.0522	0.0174	6.10662
Metolachlor	3.0001	1.0028	351.028
Cyanazine	0.6525	0.2181	76.3419

Table 16: Pesticide loads for Honey Creek, USGS04197100,
during the time interval 8404150000 to 8408150000, a span of 122 days,
during which 75 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	2.33222	2.32553	.060247
Carbofuran	6.74291	6.72359	.174186
Atrazine	80.6978	80.4665	2.08463
Terbufos	0	0	0
Fonofos	0	0	0
Metribuzin	7.6174	7.59557	.196776
Alachlor	47.3483	47.2126	1.22313
Linuron	.664561	.662657	.171673E-01
Metolachlor	46.2513	46.1188	1.19479
Cyanazine	13.5665	13.5276	.350456
Pendimethalin	2.45533	2.44829	.634273E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 119.262 days.
The monitored discharge is 14785 cfs-days, or 36.179 million cubic meters.

The total discharge during this time is 14742.7 cfs-days, or 36.0753 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 120.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 171 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 17: Pesticide concentrations for Honey Creek in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 122.203
Results based on 88 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1737	0.0581	21.2316
Carbofuran	0.2601	0.0869	31.7883
Atrazine	5.2946	1.7697	647.017
Terbufos	0.0028	0.0009	.347003
Fonofos	0.0011	0.0004	.136146
Metribuzin	0.6630	0.2216	81.0252
Alachlor	2.1271	0.7110	259.939
Linuron	0.6690	0.2236	81.7535
Metolachlor	4.4065	1.4729	538.49
Cyanazine	1.1582	0.3871	141.536

Table 18: Pesticide loads for Honey Creek, USGS04197100, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 91 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	1.06503	1.05741	.273942E-01
Carbofuran	5.00794	4.97211	.128811
Atrazine	69.8392	69.3395	1.79636
Terbufos	.307577E-01	.305377E-01	.791132E-03
Fonofos	.507882E-02	.504248E-02	.130634E-03
Metribuzin	13.5167	13.42	.347667
Alachlor	39.8674	39.5822	1.02545
Linuron	10.9928	10.9141	.282749
Metolachlor	65.12	64.6541	1.67498
Cyanazine	13.5346	13.4378	.348129
Pendimethalin	.115428	.114602	.296896E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 120.391 days.
The monitored discharge is 2948.33 cfs-days, or 7.21457 million cubic meters.

The total discharge during this time is 2927.24 cfs-days, or 7.16295 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 120.25 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 165 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 19: Pesticide concentrations for Upper Honey Creek in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.75
Results based on 35 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0011	0.0004	.128672
Carbofuran	0.0825	0.0276	9.96368
Atrazine	0.6361	0.2126	76.8143
Terbufos	0.0008	0.0003	.979583E-01
Fonofos	0.0021	0.0007	.257344
Metribuzin	0.1586	0.0530	19.1481
Alachlor	0.2867	0.0958	34.62
Linuron	0.0274	0.0092	3.30898
Metolachlor	0.6179	0.2065	74.6056
Cyanazine	0.2016	0.0674	24.3435

Table 20: Pesticide loads for Upper Honey Creek, USGS04197020, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 38 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.979229E-04	.855643E-04	.194464E-04
Carbofuran	.183825	.160625	.365057E-01
Atrazine	6.06971	5.30367	1.20538
Terbufos	.476676E-02	.416516E-02	.946627E-03
Fonofos	.195846E-03	.171129E-03	.388929E-04
Metribuzin	.748462	.654	.148636
Alachlor	3.21361	2.80803	.638188
Linuron	.272666	.238254	.541485E-01
Metolachlor	2.98445	2.60779	.59268
Cyanazine	.5167	.451488	.102611
Pendimethalin	.358543E-01	.313292E-01	.712028E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 117.941 days.
The monitored discharge is 1380.63 cfs-days, or 3.37839 million cubic meters.

The total discharge during this time is 1206.38 cfs-days, or 2.95201 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 94.75 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 127 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 21: Pesticide concentrations for Upper Honey Creek in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 121.181
Results based on 18 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0092	0.0031	1.12048
Carbofuran	0.0564	0.0189	6.83808
Atrazine	0.8327	0.2783	100.906
Terbufos	0.0000	0.0000	0
Fonofos	0.0000	0.0000	0
Metribuzin	0.0880	0.0294	10.6607
Alachlor	0.2852	0.0953	34.5576
Linuron	0.0000	0.0000	0
Metolachlor	0.3121	0.1043	37.8249
Cyanazine	0.1492	0.0499	18.0765

Table 22: Pesticide loads for Upper Honey Creek, USGS04197020, during the time interval 8404150000 to 8408150000, a span of 122 days, during which 19 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.470106E-01	.437803E-01	.995008E-02
Carbofuran	.45771	.426259	.096877
Atrazine	1.1129	1.03643	.235552
Terbufos	0	0	0
Fonofos	0	0	0
Metribuzin	.317983	.296133	.067303
Alachlor	.758534	.706413	.160548
Linuron	0	0	0
Metolachlor	1.23958	1.1544	.262364
Cyanazine	.2647	.246512	.560254E-01
Pendimethalin	.483292E-02	.450084E-02	.102292E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 117.885 days.
The monitored discharge is 1058.82 cfs-days, or 2.59093 million cubic meters.

The total discharge during this time is 986.063 cfs-days, or 2.4129 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 116.005 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 145 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 23: Pesticide concentrations for Upper Honey Creek in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 121.698
Results based on 54 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0564	0.0189	6.8688
Carbofuran	0.1183	0.0395	14.3992
Atrazine	3.7028	1.2377	450.627
Terbufos	0.0001	0.0000	.01075
Fonofos	0.0000	0.0000	0
Metribuzin	0.2611	0.0873	31.7717
Alachlor	0.2552	0.0853	31.0578
Linuron	0.0474	0.0159	5.77333
Metolachlor	1.4310	0.4783	174.147
Cyanazine	2.4145	0.8070	293.835

Table 24: Pesticide loads for Upper Honey Creek, USGS04197020, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 59 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.963748E-01	.564224E-01	.128233E-01
Carbofuran	.279561	.163668	.371973E-01
Atrazine	4.69832	2.75062	.62514
Terbufos	.284121E-03	.166338E-03	.378041E-04
Fonofos	0	0	0
Metribuzin	.431541	.252645	.574192E-01
Alachlor	.453975	.265779	.604042E-01
Linuron	.131815	.077171	.175389E-01
Metolachlor	2.32101	1.35883	.308825
Cyanazine	2.14332	1.2548	.285182
Pendimethalin	0	0	0
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 114.391 days.
The monitored discharge is 435.665 cfs-days, or 1.06607 million cubic meters.

The total discharge during this time is 255.059 cfs-days, or .624129 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 103.625 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 117 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 25: Pesticide concentrations for Rock Creek in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 117.024
Results based on 37 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0000	0.0000	0
Carbofuran	0.0609	0.0203	7.12338
Atrazine	2.5161	0.8410	294.449
Terbufos	0.0000	0.0000	0
Fonofos	0.0000	0.0000	0
Metribuzin	0.3038	0.1015	35.5525
Alachlor	0.5253	0.1756	61.4676
Linuron	0.6445	0.2154	75.4237
Metolachlor	2.9165	0.9748	341.296
Cyanazine	0.2207	0.0738	25.8273

Table 26: Pesticide loads for Rock Creek, USGS04197170, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 36 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	0	0	0
Carbofuran	.210944	.234893	.262157E-01
Atrazine	16.943	18.8666	2.10564
Terbufos	0	0	0
Fonofos	0	0	0
Metribuzin	2.69211	2.99775	.33457
Alachlor	4.62516	5.15026	.574806
Linuron	5.29239	5.89324	.657728
Metolachlor	23.1922	25.8252	2.88228
Cyanazine	.908147	1.01125	.112863
Pendimethalin	.895597E-01	.997275E-01	.111303E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 110.75 days.
The monitored discharge is 2029.93 cfs-days, or 4.96724 million cubic meters.

The total discharge during this time is 2260.39 cfs-days, or 5.53118 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 111.5 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 274 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 27: Pesticide concentrations for Rock Creek in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.493
Results based on 59 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0691	0.0231	8.32152
Carbofuran	0.1278	0.0427	15.3977
Atrazine	0.9312	0.3112	112.198
Terbufos	0.0000	0.0000	0
Fonofos	0.0000	0.0000	0
Metribuzin	0.0407	0.0136	4.90295
Alachlor	0.2491	0.0833	30.013
Linuron	0.0000	0.0000	0
Metolachlor	2.1740	0.7267	261.956
Cyanazine	0.0371	0.0124	4.47312

Table 28: Pesticide loads for Rock Creek, USGS04197170,
during the time interval 8404150000 to 8408150000, a span of 122 days,
during which 61 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	2.62026	2.63461	.294041
Carbofuran	6.17311	6.20692	.692736
Atrazine	26.3585	26.5029	2.95791
Terbufos	0	0	0
Fonofos	0	0	0
Metribuzin	.904893	.909849	.101546
Alachlor	10.9323	10.9922	1.22681
Linuron	0	0	0
Metolachlor	21.0935	21.209	2.36708
Cyanazine	2.01961	2.03067	.226638
Pendimethalin	.646228E-01	.649767E-01	.725187E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 119.764 days.
The monitored discharge is 4855.33 cfs-days, or 11.881 million cubic meters.

The total discharge during this time is 4881.92 cfs-days, or 11.9461 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 198 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 29: Pesticide concentrations for Rock Creek in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 121.674
Results based on 101 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0582	0.0194	7.07836
Carbofuran	0.2286	0.0764	27.8185
Atrazine	3.5877	1.1992	436.523
Terbufos	0.0010	0.0003	.122806
Fonofos	0.0001	0.0000	.0155
Metribuzin	0.5736	0.1917	69.7899
Alachlor	0.5646	0.1887	68.6994
Linuron	0.6879	0.2299	83.704
Metolachlor	6.6734	2.2306	811.979
Cyanazine	0.1993	0.0666	24.2469

Table 30: Pesticide loads for Rock Creek, USGS04197170, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 105 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.159376	.159949	.178515E-01
Carbofuran	.972099	.975597	.108884
Atrazine	9.82585	9.86121	1.10058
Terbufos	.266819E-02	.267779E-02	.298861E-03
Fonofos	.438666E-03	.440244E-03	.491344E-04
Metribuzin	2.23313	2.24117	.250131
Alachlor	1.78	1.7864	.199376
Linuron	1.77497	1.78136	.198812
Metolachlor	18.223	18.2886	2.04114
Cyanazine	.519935	.521806	.582373E-01
Pendimethalin	0	0	0
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 119.799 days.
The monitored discharge is 1083.67 cfs-days, or 2.65173 million cubic meters.

The total discharge during this time is 1087.57 cfs-days, or 2.66127 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 121.875 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 156 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 31: Pesticide concentrations for Lost Creek in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 118.981
Results based on 39 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0022	0.0007	.265
Carbofuran	0.0657	0.0220	7.81519
Atrazine	3.7682	1.2595	448.347
Terbufos	0.0355	0.0119	4.22753
Fonofos	0.0016	0.0005	.18617
Metribuzin	0.5862	0.1959	69.7411
Alachlor	2.3692	0.7919	281.885
Linuron	0.3666	0.1225	43.6163
Metolachlor	1.4825	0.4955	176.394
Cyanazine	0.8258	0.2760	98.25

Table 32: Pesticide loads for Lost Creek, USGS04185440,
during the time interval 8304150000 to 8308150000, a span of 122 days,
during which 40 pesticide samples were taken. (Values subject to revision.)

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.512874E-02	.457867E-02	.538668E-02
Carbofuran	.831541E-01	.742357E-01	.873361E-01
Atrazine	7.76558	6.93271	8.15613
Terbufos	.516162E-01	.460803E-01	.542121E-01
Fonofos	.347704E-02	.310412E-02	.365191E-02
Metribuzin	1.58573	1.41565	1.66548
Alachlor	5.88742	5.25598	6.18351
Linuron	.594775	.530984	.624687
Metolachlor	3.11311	2.77922	3.26967
Cyanazine	1.93489	1.72737	2.03221
Pendimethalin	.578629	.51657	.60773
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 109.753 days.
The monitored discharge is 569.545 cfs-days, or 1.39368 million cubic meters.

The total discharge during this time is 508.46 cfs-days, or 1.2442 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 63.0163 days out of 122 with each flow measurement characterizing one day or less. 6 flow values out of 234 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 33: Pesticide concentrations for Lost Creek in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 117.491
Results based on 36 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0440	0.0147	5.17228
Carbofuran	0.1160	0.0388	13.6343
Atrazine	5.6544	1.8900	664.346
Terbufos	0.0000	0.0000	0
Fonofos	0.0016	0.0005	.184479
Metribuzin	0.2470	0.0826	29.0201
Alachlor	1.7234	0.5760	202.486
Linuron	0.0000	0.0000	0
Metolachlor	0.6007	0.2008	70.5752
Cyanazine	1.5428	0.5157	181.269

Table 34: Pesticide loads for Lost Creek, USGS04185440,
during the time interval 8404150000 to 8408150000, a span of 122 days,
during which 38 pesticide samples were taken. (Values subject to revision.)

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.817506E-01	.462343E-01	.543933E-01
Carbofuran	.280967	.158902	.186944
Atrazine	23.7721	13.4444	15.8169
Terbufos	0	0	0
Fonofos	.400351E-02	.22642E-02	.266376E-02
Metribuzin	.638174	.360921	.424613
Alachlor	3.93656	2.22634	2.61922
Linuron	0	0	0
Metolachlor	.852234	.481984	.56704
Cyanazine	3.21759	1.81972	2.14085
Pendimethalin	.331997E-01	.187762E-01	.220897E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 116.745 days.
The monitored discharge is 548.96 cfs-days, or 1.34331 million cubic meters.

The total discharge during this time is 310.466 cfs-days, or .75971 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 45.9684 days out of 122 with each flow measurement characterizing one day or less. 48 flow values out of 139 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 35: Pesticide concentrations for Lost Creek in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 122.017
Results based on 37 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0101	0.0034	1.23285
Carbofuran	0.0236	0.0079	2.87943
Atrazine	0.6471	0.2163	78.9536
Terbufos	0.0001	0.0000	.013
Fonofos	0.0000	0.0000	0
Metribuzin	0.0503	0.0168	6.14306
Alachlor	0.0666	0.0223	8.13094
Linuron	0.0039	0.0013	.47225
Metolachlor	0.4110	0.1374	50.1449
Cyanazine	0.4479	0.1497	54.6473

Table 36: Pesticide loads for Lost Creek, USGS04185440,
during the time interval 8504150000 to 8508150000, a span of 122 days,
during which 44 pesticide samples were taken. (Values subject to revision.)

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.100654E-02	.397579E-03	.46774E-03
Carbofuran	.109786E-01	.43365E-02	.510176E-02
Atrazine	.079732	.314939E-01	.370516E-01
Terbufos	.190866E-05	.753915E-06	.886959E-06
Fonofos	0	0	0
Metribuzin	.843038E-02	.332997E-02	.391762E-02
Alachlor	.154783E-01	.611389E-02	.719281E-02
Linuron	.143002E-03	.564853E-04	.664533E-04
Metolachlor	.235787E-01	.931353E-02	.109571E-01
Cyanazine	.229641E-01	.907076E-02	.106715E-01
Pendimethalin	.995599E-03	.393259E-03	.462657E-03
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 118.017 days.
The monitored discharge is 38.0826 cfs-days, or .931882E-01 million cubic meters.

The total discharge during this time is 15.0425 cfs-days, or .368091E-01 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 76.75 days out of 122 with each flow measurement characterizing one day or less. 2 flow values out of 92 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 37: Pesticide concentrations for the River Raisin in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 117.599
Results based on 18 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0008	0.0003	.0895
Carbofuran	0.1715	0.0573	20.164
Atrazine	1.0671	0.3567	125.486
Terbufos	0.0280	0.0093	3.28691
Fonofos	0.0026	0.0009	.305234
Metribuzin	0.1352	0.0452	15.8997
Alachlor	0.5399	0.1804	63.4869
Linuron	0.0792	0.0265	9.31544
Metolachlor	0.3166	0.1058	37.2295
Cyanazine	0.3409	0.1139	40.0871

Table 38: Pesticide loads for the River Raisin, USGS04176500, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 19 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	.131227	.113987	.422332E-03
Carbofuran	40.1594	34.8834	.129246
Atrazine	412.29	358.126	1.32688
Terbufos	6.73803	5.85283	.216852E-01
Fonofos	.764416	.663991	.246014E-02
Metribuzin	73.576	63.9099	.236791
Alachlor	257.318	223.513	.828133
Linuron	31.386	27.2627	.10101
Metolachlor	154.639	134.323	.497677
Cyanazine	107.582	93.4487	.346235
Pendimethalin	8.12934	7.06135	.261628E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 109.87 days.
The monitored discharge is 141563 cfs-days, or 346.404 million cubic meters.

The total discharge during this time is 122965 cfs-days, or 300.896 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 103.141 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 104 were missing.

The observed loads correspond to the time and discharge monitored.
The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge.
The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 39: Pesticide concentrations for the River Raisin in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 120.5
Results based on 29 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0421	0.0141	5.06772
Carbofuran	0.0288	0.0096	3.47321
Atrazine	0.9688	0.3238	116.737
Terbufos	0.0000	0.0000	0
Fonofos	0.0202	0.0068	2.43408
Metribuzin	0.0467	0.0156	5.63188
Alachlor	0.7842	0.2621	94.4923
Linuron	0.0126	0.0042	1.51433
Metolachlor	0.4446	0.1486	53.5796
Cyanazine	0.4834	0.1616	58.2546

Table 40: Pesticide loads for the River Raisin, USGS04176500, during the time interval 8404150000 to 8408150000, a span of 122 days, during which 30 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	10.315	9.18442	.034029
Carbofuran	2.98087	2.65415	.983382E-02
Atrazine	320.642	285.499	1.05779
Terbufos	0	0	0
Fonofos	3.29257	2.93169	.108621E-01
Metribuzin	24.8124	22.0928	.818556E-01
Alachlor	270.88	241.19	.893627
Linuron	.458378	.408138	.151218E-02
Metolachlor	95.2372	84.7988	.314186
Cyanazine	199.298	177.454	.65748
Pendimethalin	2.78217	2.47723	.917833E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 116.944 days.
The monitored discharge is 86900.8 cfs-days, or 212.646 million cubic meters.

The total discharge during this time is 77376.1 cfs-days, or 189.339 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 102.937 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 103 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 41: Pesticide concentrations for the River Raisin in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 110
Results based on 15 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.1880	0.0628	20.6759
Carbofuran	0.0401	0.0134	4.40915
Atrazine	1.8062	0.6037	198.681
Terbufos	0.0000	0.0000	0
Fonofos	0.0067	0.0022	.732958
Metribuzin	0.1508	0.0504	16.591
Alachlor	1.0260	0.3429	112.859
Linuron	0.4316	0.1443	47.4775
Metolachlor	0.7873	0.2632	86.6053
Cyanazine	0.4583	0.1532	50.4184

Table 42: Pesticide loads for the River Raisin, USGS04176500, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 16 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	12.6168	12.5889	.466429E-01
Carbofuran	3.09756	3.09073	.114514E-01
Atrazine	151.834	151.499	.561314
Terbufos	0	0	0
Fonofos	.585477	.584185	.216445E-02
Metribuzin	13.7212	13.6909	.507258E-01
Alachlor	87.0336	86.8415	.321754
Linuron	25.9203	25.8631	.958246E-01
Metolachlor	68.9871	68.8349	.255038
Cyanazine	35.5808	35.5022	.131538
Pendimethalin	0	0	0
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 103.427 days.
The monitored discharge is 30744.3 cfs-days, or 75.2313 million cubic meters.

The total discharge during this time is 30676.5 cfs-days, or 75.0653 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 99.6041 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 99 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 43: Pesticide concentrations for the Cuyahoga River in 1983.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 113.298
Results based on 15 samples in the period 830415 to 830815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.0343	0.0114	3.88052
Carbofuran	0.5960	0.1992	67.5232
Atrazine	0.3583	0.1197	40.5894
Terbufos	0.0963	0.0322	10.9056
Fonofos	0.1673	0.0559	18.9564
Metribuzin	0.1742	0.0582	19.737
Alachlor	0.0904	0.0302	10.2468
Linuron	0.0903	0.0302	10.2356
Metolachlor	0.5159	0.1725	58.4559
Cyanazine	0.2924	0.0977	33.1333

Table 44: Pesticide loads for the Cuyahoga River, USGS04208000, during the time interval 8304150000 to 8308150000, a span of 122 days, during which 15 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	4.98199	5.37344	.029347
Carbofuran	161.081	173.737	.948866
Atrazine	73.7977	79.5963	.434715
Terbufos	14.291	15.4139	.841829E-01
Fonofos	13.8592	14.9481	.816392E-01
Metribuzin	21.8147	23.5288	.128502
Alachlor	13.2275	14.2668	.779182E-01
Linuron	12.4207	13.3966	.731654E-01
Metolachlor	85.2091	91.9043	.501935
Cyanazine	56.3098	60.7342	.3317
Pendimethalin	12.0116	12.9553	.707556E-01
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 100.865 days.
The monitored discharge is 109643 cfs-days, or 268.297 million cubic meters.

The total discharge during this time is 118258 cfs-days, or 289.378 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 107.5 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 141 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 45: Pesticide concentrations for the Cuyahoga River in 1984.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 83.8663
Results based on 12 samples in the period 840415 to 840815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.7405	0.2475	62.105
Carbofuran	0.1833	0.0613	15.3751
Atrazine	0.2179	0.0728	18.2751
Terbufos	0.0053	0.0018	.448
Fonofos	0.0082	0.0028	.691121
Metribuzin	0.0475	0.0159	3.98034
Alachlor	0.0958	0.0320	8.03184
Linuron	0.3799	0.1270	31.8616
Metolachlor	0.0010	0.0003	.859372E-01
Cyanazine	0.0063	0.0021	.532122

Table 46: Pesticide loads for the Cuyahoga River, USGS04208000, during the time interval 8404150000 to 8408150000, a span of 122 days, during which 14 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	132.075	148.643	.811813
Carbofuran	66.9182	75.3128	.411321
Atrazine	54.3214	61.1358	.333893
Terbufos	2.07351	2.33362	.127451E-01
Fonofos	2.71794	3.0589	.167062E-01
Metribuzin	17.7068	19.9281	.108837
Alachlor	23.0053	25.8912	.141405
Linuron	83.9372	94.4668	.51593
Metolachlor	7.8496	8.83431	.482485E-01
Cyanazine	4.32179	4.86394	.265644E-01
Pendimethalin	.541895	.609873	.333082E-02
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 85.9549 days.
The monitored discharge is 113783 cfs-days, or 278.428 million cubic meters.

The total discharge during this time is 128057 cfs-days, or 313.355 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 108.375 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 134 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

Table 47: Pesticide concentrations for the Cuyahoga River in 1985.

In the results below, the time any sample can represent was limited to 14 days.

Adjustments to the whole year were made assuming the time-weighted mean concentration characterized the monitored interval, and a concentration of 0.000 characterized the rest of the year.

Total monitored time (days) is 121.552
Results based on 16 samples in the period 850415 to 850815

Parameter	Time-weighted mean concentration (ug/L or ppb)	Adjusted to whole year	Observed flux ppb-days
Simazine	0.4415	0.1476	53.6694
Carbofuran	0.0431	0.0144	5.23406
Atrazine	0.4417	0.1477	53.6945
Terbufos	0.0000	0.0000	0
Fonofos	0.0151	0.0050	1.8352
Metribuzin	0.0000	0.0000	0
Alachlor	0.0135	0.0045	1.645
Linuron	0.1054	0.0352	12.8075
Metolachlor	0.1070	0.0358	13.005
Cyanazine	0.0949	0.0317	11.5295

Table 48: Pesticide loads for the Cuyahoga River, USGS04208000, during the time interval 8504150000 to 8508150000, a span of 122 days, during which 19 pesticide samples were taken.

The time characterized by any pesticide sample was limited to 14 days.

The loads calculated in this manner are as follows:

Pesticide	Observed Load kg	Extrapolated Load kg	Unit area Load g/ha
Simazine	84.7051	82.7257	.451806
Carbofuran	16.6353	16.2465	.887303E-01
Atrazine	100.551	98.2013	.536326
Terbufos	0	0	0
Fonofos	1.88642	1.84233	.100619E-01
Metribuzin	.303122	.296038	.161681E-02
Alachlor	2.42571	2.36903	.129384E-01
Linuron	45.8115	44.741	.244353
Metolachlor	23.5251	22.9753	.12548
Cyanazine	17.0119	16.6144	.907394E-01
Pendimethalin	0	0	0
EPTC	-------	-------	-------
DIA	-------	-------	-------
DEA	-------	-------	-------
Ethoprop	-------	-------	-------
Trifluralin	-------	-------	-------
Phorate	-------	-------	-------
Propoxur	-------	-------	-------
Aldicarb	-------	-------	-------

The monitored time is 121.052 days.
The monitored discharge is 75005.8 cfs-days, or 183.539 million cubic meters.

The total discharge during this time is 73253 cfs-days, or 179.25 million cubic meters, and is based on the most complete discharge record available in the computer. Due to differences in data and calculation approach, this discharge may differ from the USGS discharge for the same time period. The discharge record covers 120 days out of 122 with each flow measurement characterizing one day or less. 0 flow values out of 166 were missing.

The observed loads correspond to the time and discharge monitored. The extrapolated loads are calculated by multiplying the observed load by the ratio of the total discharge to the monitored discharge. The unit area load is the extrapolated load divided by the watershed area and re-expressed as grams per hectare.

The accuracy of the load estimates is dependent on the frequency and representativeness of the pesticide samples and the flow data. Infrequent pesticide samples are more often the limiting factor than is inadequate flow data.

Pesticide concentrations below detection limit are taken as 0.000 ug/L.

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